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Beyond the local-density approximation in calculations of ground-state electronic properties

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Justification, as extensive as is possible, is given for our previously published nonlocal approximation for exchange and correlation. Some new exact limits for atoms and interfaces are obtained, as well as formal quantitative criteria for the validity of the local-density approximation and the gradient corrections to it. The scheme is applied to planar surface calculations, as well as to extensive self-consistent calculations of energies and densities in atoms. The results compare favorably, in every case attempted, to experimental and exact results that are available. A method is devised for separating exchange from correlation in atoms within the Kohn-Sham method, and is tested favorably against exact-exchange calculations. Finally, we apply these results to atoms using exact exchange plus our appropriately separated correlation expression. The results give atomic total energies to accuracies of $\sim \pm 0.01$ Ry, and typically reduce the local-density-approximation error in density by an order of magnitude.

I. INTRODUCTION

Previously, the present authors[1] (this work hereafter referred to as LM) proposed a workable calculational scheme for including the effects of exchange and correlation beyond the local-density approximation[2] (LDA) in nonuniform systems such as atoms, solids, molecules, surfaces, etc. This was based on a mode of approximation introduced to such systems by Langreth and Perdew[3-6] and by others.[7-9] LM was based to a large extent on the work of Langreth and Perdew[6] (hereafter referred to as I) and the type of approximation scheme introduced there. This earlier scheme and its relation to the work of other authors such as Gunnarsson, Jonson, and Lundqvist,[10] Alonso and Girifalco,[11] Gunnarsson and Jones,[12] and Kohn and Hanke[13] have been aptly reviewed recently by Williams and von Barth[14] whose work relieves us of the burden of a detailed discussion here. More recently, Perdew and collaborators[15-17] have revived, and elaborated on, methods for correcting for self-interactions, and we will mention aspects of this related work later.

The present work has a number of aims. The first is to give, in Sec. II, as complete a justification as we are able for the calculational scheme introduced in LM. In the process, we obtain some results and reach some conclusions that are interesting in their own right: In Sec. II B, we derive the long-wavelength limit of the exchange-correlation energy for (a) atoms and other finite systems and (b) for planar interfaces in metals; in Sec. II C, we develop sufficient *a priori quantitative* criteria for the LDA to be a good approximation, as well as for the first-order gradient approximation to give an accurate correction to the LDA; we find that the criterion for the former is considerably less severe than often supposed and, as previously discussed,[1,6] that the criterion for the latter (gradient) is not only more severe than previously supposed, but also considerably more severe than the criterion for the former (LDA). We find that our *a priori* criterion for the LDA's validity *is* roughly satisfied for a wide variety of systems (while that for the gradient corrections to it is generally not), thus resolving a paradox which was the apparent motivation for others such as Gunnarsson and Lundqvist[18] to seek reasons other than the satisfaction of *a priori* criteria for the huge success[14,19,20] of the LDA in practice. Of course, we do not disagree with Gunnarsson and Lundqvist's reasons, i.e., that the spherical average of the exchange-correlation hole along with its obeying of the sum rule improves things: These facts are reflected in the quantitative *a priori* criteria which we give, making them less severe than they otherwise would have been.

In Sec. II A we discuss the true exchange-correlation *functional* as a simple *function* of a multitude of wave vectors and argue that in a qualitative sense at least there is only one of these in addition to k_F (the local Fermi wave vector) which is most important. This notion, along with a number of exact limits (which are added to in Sec. II B), are used in Sec. II C to develop and to justify as far as possible the LM approximation scheme.

In Sec. III we apply the scheme to planar surfaces as well as to atoms. In addition to the calculation in LM, we calculate atomic densities and compare them with the exact ones for the spinless atoms through Ar. Our approximation reproduces all the trends in predicting the error in the LDA and goes a long way in making the densities more like the exact ones. We examine the exchange-correlation potential v_{xc} for our approximation in Sec. III F. This has the cusplike features at the proper positions between the orbitals and strengths similar to what the exact-exchange potentials[21–23] have. The results for the densities as well as for the potentials give strong evidence that our scheme is basically correct. We also argue that the Kohn-Sham eigenvalue *differences* for occupied states are very close to the exact ones, in agreement with the recent observation of Perdew and Norman[24] that this is incontrovertibly true for the local-density approximation to exchange only.

In Sec. IV we propose an approximate and somewhat speculative method for separating exchange from correlation. This method happens to work well for all properties tested in atomic calculations, including total energies, exchange energies, densities, and Kohn-Sham eigenvalues; when combined with the calculations in Sec. III, it gives excellent results for correlation energies. It becomes clear from the calculations in this section that the largest source of error in the approximate LM scheme is its treatment of exchange, and *not* the details of the somewhat crude small wave-vector cutoff procedure for correlation.

The motivation for separating exchange and correlation is, of course, the longstanding one: Exchange alone can be computed exactly and, for localized nondegenerate systems, rather simply.[21–23,25] Exact exchange may then be combined with an approximate expression for correlation,[26] as is done in Sec. V, and then applied to atoms. This results in a spectacular improvement in energies and densities when compared with the LDA.

In summary then, we feel that the evidence is strong that the original LM scheme is basically correct, and should give substantial improvements in the predicted ground-state properties of a wide variety of systems, and we recommend its use for calculations of energies, densities, elastic properties, and so on, especially for bulk materials, and probably also for surfaces. It should also be expected to give improved eigenvalue differences for occupied states over the LDA; these changes in eigenvalues will not be large, however—and correctly so, we believe—since the LDA already seems to be an excellent approximation to the eigenvalue differences of the Kohn-Sham equations using the exact potential.

It would seem important from a theoretical point of view to investigate further the question of separating exchange and correlation, to which the idea introduced in Sec. IV represents a start. Of particular importance is the question of whether and/or how this notion can be generalized to calculations involving more delocalized states than those of atomic orbitals. If the numerical success of Sec. V could be extended to small molecules and clusters, this would be a major advance indeed.

II. THE LM CALCULATIONAL SCHEME

A. The nonlocal exchange-correlation energy—the variables on which it depends and its behavior

We begin by writing the exchange-correlation energy of a nonuniform system in slightly unusual notation, which we hope will serve to make the size of various terms transparent:

$$E_{\mathrm{xc}}[k_F]=\frac{e^2}{4\pi^3}\int d^3r\, k_F^4 W[k_F] \;. \tag{2.1}$$

We use the local Fermi wave vector

$$k_F=k_F(\vec{r})=[3\pi^2 n(\vec{r})]^{1/3}$$

as the basic variable, instead of $n(\vec{r})$, so that E_{xc} and W are functionals of $k_F(\vec{r})$. The quantity W defined by (2.1) is then a dimensionless quantity of order unity, which we write as

$$W[k_F]=W_{\mathrm{LDA}}(k_F)+\delta W \;, \tag{2.2}$$

where W_{LDA}, a function of k_F, is the value of W in the local-density approximation[2]:

$$W_{\mathrm{LDA}}(k_F)=-\epsilon_{\mathrm{xc}}/\epsilon_x=-(1+\epsilon_c/\epsilon_x) \;, \tag{2.3}$$

where ϵ_{xc} is the sum of the exchange energy per particle $\epsilon_x=-3e^2k_F/4\pi$ and the correlation energy ϵ_c per particle for a uniform electron gas of Fermi wave vector k_F.

The deviation from the local approximation, δW, is a functional of $k_F(\vec{r})$, which can be thought of alternatively—and, for our purposes, more conveniently—as a function of a (presumably infinite) number of variables $q_1,q_2,\ldots,q_n,\ldots,$ which are determined from $k_F(\vec{r})$ as a function of $\vec{r}$ in some prescribed way; these can, without loss in generality, be taken to be inverse lengths. One of these, which may be taken as q_1, is the local k_F itself. What are the others? In the present language the problem of going beyond the local-density approximation is tantamount to identifying which inverse lengths (other than k_F) derivable from a density distribution have the greatest effect on the system's exchange-correlation energy.

Intuitively, one has the notion that if the density is varying, then it is those lengths which define the scale, over which the density varies, which are most important. For example, for a planar metallic surface, it must surely be that in addition to k_F^{-1} the next important length is the width or healing length of the surface layer. In a tightly bound orbital in an atom, molecule, or solid it must be the size of that orbital; in slowly varying valence states, such as in a solid, it presumably can be related to the derivative of the density. The main purpose of this work is to present a quantification, albeit crude, of the above intuitive notion.

Our first basic assumption is that, to fair approximation, there is just *one* length ξ for each $\vec r$, which characterizes the *scale* over which the density varies, as discussed in the above paragraph. In terms of the q's, this means that $q_1=k_F$, $q_2\simeq q_3\simeq q_4\simeq\cdots\simeq\xi^{-1}\equiv q$, and that all the remaining q's not included in the assumed approximate equalities above are unimportant. We therefore rewrite (2.2) as

$$W[k_F]\simeq W(k_F,q)\equiv W_{\rm LDA}(k_F)+Z(k_F,q)\frac{q^2}{k_F^2}\,, \tag{2.4}$$

where we have factored out q^2/k_F^2 to exhibit explicitly the trivial fact that the local-density approximation is exact when $q\to 0$. The function $Z(k_F,q)$ is a dimensionless quantity which is demonstrably of order unity (or smaller), in many cases of interest, and which will be assumed to be of this order in all the cases with which we deal here. Since $W_{\rm LDA}$ has been constructed to be of order unity, then the criterion for the validity of the LDA in this language is $q\ll k_F$, and the fractional correction to the LDA is $\sim q^2/k_F^2$. This is in accord with our experience in the examples of the above paragraph.

Next we need a measure of $q=q(\vec r)$ for a given density distribution. If our assumption that there is only one important length ξ (aside from k_F^{-1}) associated with each $\vec r$ point is sufficiently accurate, then it should not be of much consequence which of many possible physically reasonable schemes is used to evaluate it. As in our earlier preliminary report,[1] we choose the simplest reasonable possibility:

$$q(\vec r)\equiv 1/\xi=|\vec\nabla k_F(\vec r)|/2k_F(\vec r)\,. \tag{2.5}$$

This scheme has the advantage that is exact for sufficiently slowly varying disturbances when substituted into (2.4). In the latter case one may set $q=0$ in $Z(k_F,q)$ and Z may be evaluated according to the gradient expansion[27,28,5,6]; the factor of 2 in the denominator of (2.5) was chosen to make $Z(k_F,0)$ agree with previous definitions.[6,28] Note that[6,27,28] $Z(\infty,0)=1.198$ and calculations based on the random-phase approximation (RPA) and beyond do not show substantial deviation from this for any k_F of interest. The most important variation in $Z(k_F,q)$ comes from its dependence on q. As shown previously,[1,6] Eq. (2.5) also gives reasonable results for surfaces, where it predicts that ξ is on the order of the surface healing length when $\vec r$ is in the surface layer. It is also clear that (2.5) gives a ξ roughly equal to the radius of an atomic orbital when $\vec r$ is such that the density is dominated by that orbital.

Generally speaking, we feel that our success with using the simple equation (2.5), as well as the assumption of a single ξ, results in large degree from the fact that we are dealing with systems in equilibrium, or nearly in equilibrium, under their own internal forces resulting from the Coulomb interaction. Density variations with length scales grossly inconsistent with (2.5) probably do not occur in such systems.

The determination of the variation of Z with q is facilitated by making a wave-vector decomposition of $E_{\rm xc}$, as used by Nozières and Pines[29] for the uniform case and by Langreth and Perdew[3–6] plus a number of others[7–9] for the nonuniform case. This may, as in our previous work, be defined in terms of the coupling-constant integral of the exact structure factor $S_\lambda(\vec k)$ in the presence of an external potential whose coupling-constant dependence is such as to keep the spatial density variation independent of the coupling constant[3,4,18,30]

$$E_{\rm xc}(k)=\int_0^1 d\lambda(2\pi e^2/k^2)N[S_\lambda(\vec k)-1]\,. \tag{2.6}$$

We introduce the particle number N to make our normalization of $[S_\lambda(\vec k)-1]$ agree with that commonly used by others. Then we define $z(k_F,q;k)$, the wave-vector decomposition of $Z(k_F,q)$, by the equation

$$p(k)E_{\rm xc}(k)=\frac{e^2}{4\pi^3}\int d^3r\,k_F^4\left[\frac{p(k)\epsilon_{\rm xc}(k)}{\epsilon_x}+z(k_F,q;k)\frac{q^2}{k_F^2}\right], \tag{2.7}$$

where the phase-space factor

$$p(k)=4\pi k^2/(2\pi)^3$$

and

$$\epsilon_{\rm xc}(k)=\int_0^1 dx\,(2\pi e^2/k^2)[S_\lambda^B(k;k_F(\vec r))-1]\,, \tag{2.8}$$

where $S_\lambda^B(k;k_F(\vec r))$ is the structure factor for a uniform (bulk) electron gas with wave vector k_F. Of course, for $q=0$, Eq. (2.7) reduces to just $p(k)E_{\rm xc}^{\rm LDA}$, the value of $p(k)E_{\rm xc}(k)$ in the local-density approximation. Although z in (2.7) is dependent on the direction of $\vec k$, this property does not affect the energy, so that

$$Z(k_F,q)=\int_0^\infty dk\, z(k_F,q;k)\ . \tag{2.9}$$

Note that the k integral of either z or $p\epsilon_{xc}(k)/\epsilon_x$ taken separately is of order unity, at least for small q, and the degree of nonlocality is expressed by the q^2/k_F^2 factor in (2.7).

To find a viable approximation scheme for z, we begin by looking at special cases that we can solve exactly. There exists one system where there rigorously exists only one q (other than k_F) characterizing the density, and that is an otherwise uniform electronic system perturbed by a weak sinusoidal potential of wave vector q. Unfortunately, Eq. (2.5) would not provide a reasonable measure of q in this case unless the amplitude were large, and that could vitiate our assumption that treating the disturbance by perturbation theory is a valid procedure. Nevertheless, we are going to be forced to extrapolate anyway, because in practice it is always large disturbances from uniformity which we wish to treat by the methods developed here. Furthermore, Eq. (2.5), when combined with (2.4), gives a *rigorous* result for small q; then it is just the gradient expansion, which in turn may be rigorously obtained by the perturbation expansion of this paragraph. We will argue that this small-q case represents the most important contribution to z over a substantial part of the k range.

The behavior of $z(k_F,q;k)$ for small q has been implicitly derived for this model by Langreth and Perdew[6] (I) and discussed explicitly more recently.[31] Essentially, z varies with k over three wave-vector scales: The first is set by k_F, the second by the Fermi-Thomas wave vector k_{FT}, and the third by q. The Fermi-Thomas wave vector k_{FT} is not a separate "q" in the sense of the discussion following Eq. (2.3), since it is a simple function of k_F $[(k_{\mathrm{FT}}/2k_F)^{-2}=\pi a_0 k_F]$ for all points $\vec{r}$. Although there is cancellation at small wave vectors between correlation and exchange, this is less important than for the local approximation, and it makes more sense to discuss these pieces separately when considering the nonlocal contributions to z, especially since the way each of them scales with the k_F, k_{FT}, and q is different. Thus we let $z=z_x+z_c$. We show a sketch of z_c vs k in Fig. 1(a) to illustrate this scaling. Here, as elsewhere in this paper, we take the assumption $q \ll k_F$ to be a reasonable starting point, even though it may not be rigorously satisfied everywhere. Therefore, the large-k parts of Fig. 1(a) are just those of the second-order gradient approximation and could be obtained from combining the longitudinal and transverse parts of Fig. 6 in I. For k smaller than $\sim q$, however, the result (exact for the linear-response case) differs greatly from the gradient approximation, according to Eqs. (4.16) and (2.43) of I. For this small-k region we see that $z_c(k)$ becomes small ($\propto k^2$) rather than continuing upward as the dashed line in Fig. 1(a), which represents the contribution of the lowest-order gradient approximation. Effectively then the contribution at small k is cut off when $k \lesssim q$. This feature is rather general. Specifically,

$$(2k_F)z \propto k^2/q^2 \tag{2.10}$$

at small q in the normal case, and at worst $z_{\mathrm{xc}} \propto k/q$. This is important because we will later make the (fairly crude) approximation that z is effectively zero for $k \lesssim q$.

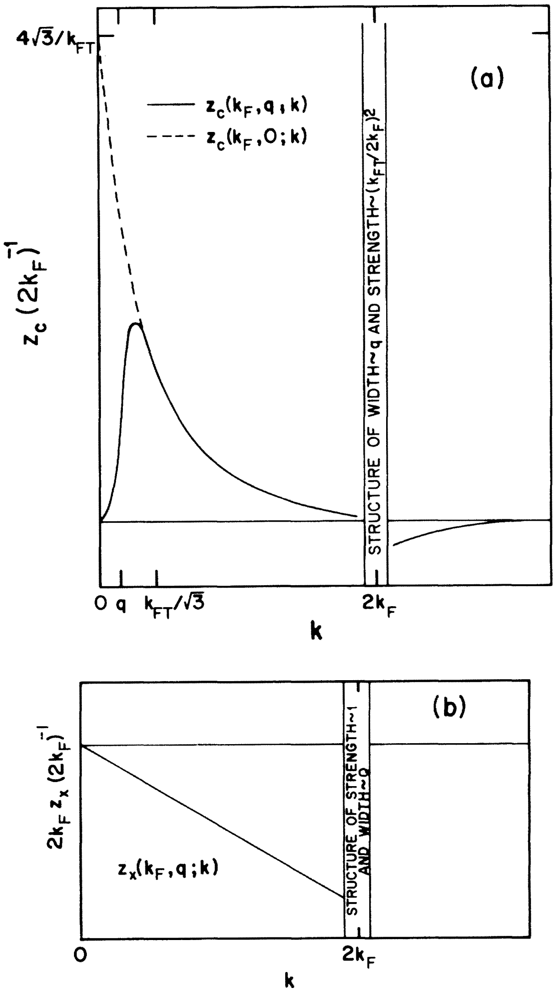

FIG. 1. Nonlocal contribution z to the exchange-correlation energy. (a) The nominal correlation contribution; the dashed line (continuing as solid) is the RPA calculation (Ref. 6) for $q=0$. The solid line for $q\neq 0$ exhibits the correct scaling features and small-q behavior, but its exact form for intermediate k is not known. (b) The nominal exchange contribution. The curve shown is exact for $q=0$ and is expected to be a reasonable approximation for $0<q\ll 2k_F$.

In Fig. 1(b) we show the form of $z_x(k)$. Essentially, we have just replotted the results for the second gradient approximation [see Eq. (3.55) of I], which is valid when our working assumption $q \ll 2k_F$ is satisfied. The extra variable q has little effect in this case: It broadens the structure for $k \sim 2k_F$. It also affects the curve near $k \sim 0$, but since z_x is small there anyway, we neglect this. We note also that the correlation piece $z_c(k)$ has a piece which exactly cancels the nonanalytic ($\propto |k|$) exchange piece at very small k. This too is an effect which is finer than the level of approximation which we ultimately make, and so we neglect it too. For practical purposes then the nonlocal exchange is nearly independent of q and equal to the area under the curve in Fig. 1(b), which is $-\frac{7}{9}$, in agreement with the calculation of Sham.[32] On the other hand, the area under the correlation curve $z_c(k)$ of Fig. 1(a) is heavily dependent on the value of q relative to the intrinsic screening length $k_{\rm FT}$. For high densities such as in the inner shells of the atoms, one has $k_{\rm FT} \ll 2k_F$, so that $q > k_{\rm FT}$, leading to a very small nonlocal correlation energy, relative to the nonlocal exchange contribution; this is just what one expects. On the other hand, at lower densities, as in the valence states of atoms and solids, one has $k_{\rm FT} \sim (2k_F)/3$ and $q \sim k_{\rm FT}$, so that although the nonlocal correlation energy is still substantially reduced from what the lowest-order gradient approximation would predict, it is still comparable to the nonlocal exchange energy. Again, this is in accord with our experience and expectations.

B. Exact results at small k

The discussion of the preceding section suggests that there is a cutoff behavior in $z_{\rm xc}(k)$ at small k, where for $k \lesssim q$, the contribution is much smaller than, for example, the lowest gradient approximation would suggest. Here we give examples where we can prove that this view is exact.

The first example is an atom or other system of finite extent. Instead of z, in this case it is simpler to discuss the quantity

$$p(k)[E_{\rm xc}(k)+2\pi e^2/k^2]$$

[see (2.7)]. If at small k it is $\propto k^2$, then z must also be $\propto k^2/q^2$, because the quantity

$$p(k)[\epsilon_{\rm xc}(k)+2\pi e^2/k^2]$$

is always $\propto k^2$. The term $2\pi e^2/k^2$ is just the interaction of a point particle with itself; it always occurs in the same manner in the local and nonlocal theory and is properly subtracted off in the definitions (2.5) and (2.7). Here we add it back again to isolate the leading terms at small k which are approximation dependent.

To evaluate $E_{\rm xc}(k)$ at small k we use (2.6) along with

$$NS(\vec{k})=\langle \delta n_{\vec{k}}\,\delta n_{-\vec{k}}\rangle\ , \qquad (2.11a)$$

where

$$\delta n_{\vec{k}}=\sum_j (e^{-i\vec{k}\cdot\vec{r}_j}-\langle e^{-i\vec{k}\cdot\vec{r}_j}\rangle)\ . \qquad (2.11b)$$

Here $\vec{r}_j$ is the position operator for the jth particle. For a finite system (2.11a) can simply be expanded in a power series at small k. Therefore,

$$NS(\vec{k})\rightarrow\vec{k}\cdot\langle\vec{d}\,\vec{d}\rangle\cdot\vec{k}\ , \qquad (2.12)$$

where

$$\vec{d}=\sum_j(\vec{r}_j-\langle\vec{r}_j\rangle)=\int d^3r\,\vec{r}\,[n^{\rm op}(\vec{r})-n(\vec{r})] \qquad (2.13)$$

is the first moment of the density operator measured from the center of charge. Since only the spherical average enters the final result, we replace the right-hand side of (2.12) by $\frac{1}{3}k^2\langle d^2\rangle$ and use (2.6), obtaining

$$p(k)\left[E_{\rm xc}(k)+\frac{2\pi e^2N}{k^2}\right]=(e^2/3\pi)\langle\langle d^2\rangle\rangle k^2\ , \qquad (2.14)$$

where $\langle\langle d^2\rangle\rangle\equiv\int_0^1 d\lambda\langle d^2\rangle$. The quantity $\langle\langle d^2\rangle\rangle$ is related to the exact polarizability, specifically

$$\langle d^2\rangle=(3/\pi e^2)\int_0^\infty\alpha_2(\omega)d\omega\ ,$$

where $\alpha_2(\omega)$ is the dissipative part of the dipole polarizability. This may be expressed as an integral up the imaginary axis of the analytic polarizability function in the usual way. Using standard exact results[4,33] we have also in the local-density approximation

$$p(k)\left[E_{\rm xc}^{\rm LDA}(k)+\frac{2\pi e^2N}{k^2}\right]=\frac{k^2}{4\pi^2}\int d^3r\,\hbar\omega_p(\vec{r})\ , \qquad (2.15)$$

where $\omega_p(\vec{r})$ is the local-plasma frequency

$$\omega_p^2=(4\pi e^2/3\pi^2 m)k_F^3\ .$$

Combining (2.14) and (2.15) clearly implies that

$$2k_FZ\propto k^2/q^2\ ,$$

in agreement with (2.10). Thus it is clear that for $k\lesssim q$, the quantity $2k_Fz$ becomes much smaller than its average value (of ~ 1 if $q\lesssim k_{\rm FT}$), thus reconfirming the picture presented in Fig. 1.

Another case where one can derive an exact result is when the nonuniformity is produced by a planar potential [$V(\vec{r})$ depending only on z, for example] of arbitrary strength applied to a uniform electron gas. This could represent an interface between two metals [$V(z=\infty)\neq V(z=-\infty)$], a surface [$V(z=\infty)\rightarrow\infty$], or simply an "impurity" of infinite extent in the x and y directions [$V(z=\infty)=V(z=-\infty)$]. The derivation is similar to that of Ref. 4 and the details will be presented in a planned future paper. The result is that for the change, $\delta E_{\mathrm{xc}}(k)$ in $E_{\mathrm{xc}}(k)$ is

$$p(k)\delta E_{\mathrm{xc}}(k)=(A/8\pi)[\omega_I-\tfrac{1}{2}(\omega_+ + \omega_-)]k + O(k^2)\ , \tag{2.16}$$

where A is the cross-sectional area of the material. Here

$$\omega_{\pm}^2=\frac{4\pi e^2}{m}n(\pm\infty)$$

are the bulk-plasma frequencies for the densities n at $z=\pm\infty$, respectively, and ω_I is the frequency (at long wavelength) of the interface mode

$$\omega_I^2=(\omega_+^2+\omega_-^2)/2\ . \tag{2.17}$$

Equation (2.16) may be interpreted physically in the same way as the analogous results for a planar surface,[4] that is, as a shift in zero-point energies. In the most general case, (2.16) is an exception to (2.10), as it implies that $z\propto k$ rather than k^2. Nevertheless, it is still greatly reduced from the finite value of z implied by the dashed curve in Fig. 1(a), and qualitatively closer numerically to the solid curve. Notice, however, that it takes a rather extreme nonuniformity to produce even this deviation, that is to say, a nonuniformity which has infinite extent in all three spatial directions. The interface ($\omega_+\neq\omega_-$) and the surface ($\omega_-=0$) are of this type. However, a nonuniformity of infinite extent only in two spatial directions corresponds to (2.16) with $\omega_+=\omega_-$. In this case the quantity in the square brackets in (2.16) vanishes so that

$$p(k)\delta E_{\mathrm{xc}}(k)\rightarrow O(k^2)\ ,$$

and so that (2.10) holds.

In summary then we have shown that $z\propto k^2$ at small k for (a) any finite system, (b) a weak periodic nonuniformity in an infinite system (and we suspect any periodic nonuniformity), and (c) a planar nonuniformity in an infinite system which does not extend an infinite distance in the z direction (in a nonperiodic manner). This means that for any finite nonuniformity, $z\propto k^2$ as well. For a planar surface or interface, (2.10) fails, but in a rather innocuous way for our purposes, $z\propto k$.

C. Development of a viable approximation scheme that is simple enough to apply in practical situations

Within the context of our single-q approximation discussed earlier, it is clear from (2.4) or (2.7) that the criterion for the validity of the local-density approximation is $q \ll k_F$, since $\epsilon_{\mathrm{xc}}/\epsilon_x$ and Z are each of order unity by construction. For constructing this criterion we may clearly use then q of (2.5) since it is rigorously this q above that determines the leading correction to the LDA. Then the fractional correction to the LDA [see (2.4)] is expected to be of order

$$\delta\equiv\frac{q^2(\vec{r})}{[k_F(\vec{r})]^2}=\left[\frac{\vec{\nabla}k_F(\vec{r})}{2[k_F(\vec{r})]^2}\right]^2\ . \tag{2.18}$$

As an example, consider the 1s state in Be which has a mean radius of $\sim$0.41 a.u. At this radius the electron density $n\sim1.5$ a.u. and $|\vec{\nabla}n(\vec{r})|\sim11$ a.u. This leads to $\delta\sim12\%$. On the other hand, the LDA for Be gives a total energy which is in error by $\sim$0.3–0.4 Ry depending on the precise form of the LDA used. However, the exchange-correlation energy (E_{xc}) of Be is around 5 Ry. Therefore, $\Delta E_{\mathrm{xc}}/E_{\mathrm{xc}}\sim$6–8 %, which is consistent with the δ of $\sim12\%$ calculated from (2.18) (this comparison is a reasonable one because most of the absolute error in the total energy as well as most of E_{xc} comes from the 1s orbital).

Equation (2.18) thus provides a *quantitative* estimate of when the LDA is valid. On the one hand, it is remarkable that one can extrapolate to situations different from that (a nearly uniform electron gas) where the equations were derived, *but* on the other hand, one should note that (2.18) is less severe by a numerical factor than criteria often seen in the literature. We *assume* it to be valid or on the verge of being valid for $\vec{r}$'s of consequence in all that follows. Thus we deal here only with the question of how to improve things when the LDA is a reasonable starting point, as it seems to be *de facto* in a large number of atoms, molecules, and solids.

The next question is when does the lowest gradient approximation [dashed curve in Fig. 1(a)] provide a reasonable approximation to the exact correction to the LDA? The approximation of a single q is of course not exact, but is physically reasonable and should be thought of more globally than as a derivative at a point, even though we use (2.5) as a measure of it. Technically of course, one must consider higher derivatives of the density, especially if one insists on viewing the density only on a semilocal basis. It is not expected or even physically reasonable in most cases that these should introduce

q's vastly different from (2.5), at least if one is willing to smooth over rapid charges in the potential as the Schrödinger equation automatically does. In any case, higher derivatives would be of no use unless one could calculate the next term in the gradient series, a feat which is currently way out of reach. In any case we prefer to think of the single-q approximation, as given by (2.5), as a crude, but nevertheless physically reasonable, approximation to a truly globally nonlocal functional rather than as a term in a "semilocal" expansion of derivatives. It is an approximation, however, whose error we cannot quantify, except by comparing our results with experiment or with virtually exact numerical solutions in certain cases.

Assuming now that the single-q approximation is acceptable, we can then get back to the originally posed question of when the dashed curve in Fig. 1(a) is a good approximation. Obviously, one must have $q \ll k_F$, but there are now more k's with which to compare q. In particular, one must have $q \ll k$ itself, or else, as our previous discussion concluded, the easily calculated dashed curve must be replaced by the solid curve whose general behavior is known, but for which exact calculations exist only for very small k. It is obvious that the area under the two curves is substantially different unless q is very small indeed, that is, *very* much smaller than k_{FT}. For example, in I $q \ll k_{\mathrm{FT}}/6$ was estimated to be the criterion. This is generally not satisfied in real systems of interest.

Therefore, one is forced to consider the difference between the two curves in Fig. 1(a), and in particular to use the solid one. In particular, it is not a viable procedure to put $q \rightarrow 0$ in the $z(k_F,q;k)$ of Eq. (2.7) even though $q \ll k_F$ and the LDA is a reasonable first approximation. This is of course why attempts to apply lowest-order *a priori* gradient expansions for exchange and correlation to physical systems are bound to fail, and often even fail to get the right sign for the correction.

We now are in a position to describe our approximation procedure for z. It is in a sense crude, but because it contains what we feel is the correct physics as described above, we feel it is a viable one; and we find that it gives a substantial improvement over the LDA.

The procedure is as follows. First, for $k > k_c$, where $k_c \sim q$, we simply set $q=0$ in $z_c(k_F,q;k)$. This procedure is valid for $k \gg q$ because of our assumption that $q^2 \ll k_F^2$. We are, nevertheless, extrapolating when $k \sim q$. We make a more extreme approximation for $k < k_c$, that is, we take $z_c(k_F,q;k)=0$ for $k < k_c$. This is correct at $k \rightarrow 0$ according to Fig. 1 and also according to the exact results in Sec. II B. For $0 < k < k_c$ this represents the obvious fact that $z_c(k_F,q;k) \ll z_c(k_F,0;k)$, but of course fails to give its precise value. Indeed, to do better is probably not possible in our single-q approximation, because the exact form as a function of k depends on the type of system (a surface is different from an atom); this is not a failure of universality but rather just an indication that more q's are necessary to describe the system precisely in this region.

We therefore state our approximation to z_c as

$$z_c(k_F,q;k)=z_c(k_F,0;k)\Theta(k-k_c)\ , \tag{2.19}$$

where Θ is the unit step function. This presumably provides an overestimate of z_c for k slightly larger than k_c and an underestimate for k slightly smaller than k_c, so that the proper behavior (2.9) can be mimicked in the simple cutoff approximation by choosing k_c properly. To be consistent with our early notation in LM we let $k_c=6fq$, where f is adjustable. In LM we gave a short and crude argument that $f \simeq \frac{1}{6}$ was the approximate value to be expected, that is, $k_c=q$ exactly. We still agree with this value and preliminary tests where f was stepped in increments of 0.05 led us to choose $f=0.15$, which is very close to $\frac{1}{6}$. More extensive tests revealed that slightly smaller values of f (such as $f \sim 0.13$) were better for surfaces while slightly larger ones (such as $f \sim 0.17$) were better for atoms. This is to be expected because for surfaces a smaller value provides a mock-up (however crude) of the $z \propto k$ dependence at small k which is completely wiped out by the cutoff approximation (2.9). In any case we present our results here with the same value $f=0.15$, which we adopted over two years ago. To summarize them we take

$$k_c=6fq=3f\,|\,\vec{\nabla}k_F(\vec{r})/k_F(\vec{r})\,|=f\,|\,\vec{\nabla}n(\vec{r})/n(\vec{r})\,| \tag{2.20}$$

with $f=0.15$.

In making the approximation (2.19) we have made a little mistake, in principle, which we have not yet discussed. The vast difference between the two curves in Fig. 1(a) at small k occurs from the differing small-k behaviors of the "fluctuation" contribution to z as displayed in Eqs. (4.8) and (4.16) of I. The quantity z also has two other sections [see (3.53) of I] which do not have a large small-k contribution even if $q \rightarrow 0$. The Hartree-Fock–type section has a section which exactly cancels out the nonanalytic dependence of z_x at small k ($z_x \propto |\,k\,|$). By subjecting the Hartree-Fock–type piece to the cutoff procedure on the same grounds as the fluctuation term, we have destroyed the former's ability to cancel this dependence ($\propto |\,k\,|$) in the exchange term. This is a small error, however, (because it occurs in a small term which vanishes as $k \rightarrow 0$ in addition) and we neglect it. This presumably leads to an error much smaller than the step-function cutoff on the much larger fluctuation terms. To do otherwise leads to technical problems that are very cumbersome to handle (involving preserving cancellations of divergences at $2k_F$ as well as finding analytical approximations to the more complicated expressions that result). Alternatively, one could put some sort of cutoff on small k in the exchange term; but this, aside from questions of principle, leads to cumbersome expressions. In summary, attempts to eliminate this error have been abandoned as not worth the small improvement they might make.

Thus we approximate

$$z_x(k_F,q;k)\simeq z_x(k_F,0;k) \tag{2.21}$$

for all q, where $z_x(k_F,0;k)$ was calculated in Eq. (3.55) of I and given in the point form by Eq. (9) of LM:

$$2k_F z_x(k_F,0;k)=-4x\Theta(1-x)+\tfrac{11}{9}\delta(x-1)+\tfrac{1}{9}\delta'(x-1)\ , \tag{2.22}$$

where $x=k/2k_F$. Since this is independent of q, we find from (2.9), for exchange only,

$$Z_x(k_F,q)=-\tfrac{7}{9}\ , \tag{2.23}$$

independent of q and k_F. This is just the value from the lowest-order gradient approximation and agrees with Sham's[32] calculation. Its k_F and q independence means that according to (2.1) the exchange contribution has the scaling property that if all lengths are increased by a factor of α, then this contribution decreases by a factor of α^{-1}, that is, it is proportional to e^2/α, which is to be expected of exchange involving the Coulomb interaction.

Return now to the discussion of z_c according to (2.19). The necessary quantity $z_c(k_F,0;k)$ has been calculated in lowest-order RPA by Langreth and Perdew.[5,6] A similar calculation has been made in the same approximation by Rasolt and Geldart.[9] The results of the calculation by the two groups agree in their general features but differ in quantitative detail. We believe that this difference is due to a difference in definition of the wave vector k between the two groups, as discussed in Ref. 31. The integrated z_c's agree almost exactly. The arguments in the present paper are crucially dependent on the wave vector k being identical to the wave vector in the structure factor [see Eq. (2.6)]. This correspondence was rigorously maintained in the Langreth-Perdew calculation and this is what we adopt here.

An important simplifying result is that the integrated z_c has a value very close to 2 almost independent of density (at least for $k_F \gtrsim 0.5$ a.u.). This is in agreement with Ma and Brueckner's value of 1.976, which corresponds to $k_F\rightarrow\infty$. In this connection the question of higher-order contributions within the RPA is still not completely settled. Langreth and Perdew[5,6] included these terms in principle but argued that to a good approximation they cancelled exactly. Rasolt and Geldart[28] had previously also found approximate cancellation, but it was not complete, and therefore the resulting z_c had a stronger density dependence (although still rather weak). This would lead to a change which is perceivable, although slight, in the results which we present later using the Langreth-Perdew[5,6] expressions (I).

The analytic expressions in I for $z_c(k_F,0;k)$ are lengthy and require an additional integration before the final wave-vector decomposition is obtained. Therefore, in order to implement (2.19) in a practical density-functional scheme it was necessary to have an analytic parametrization of it. We were guided by the near constancy of z_c with density (we take $z_c=2$ at all densities) in addition to the fact, derived in I, that

$$\lim_{k\to 0} z_c(k_F,0;k)=4\sqrt{3}/k_{\rm FT}\ . \tag{2.24}$$

Since the dashed curve in Fig. 1(a) appears similar to an exponential (for $k\lesssim 2k_F$) we simply tried that exponential consistent with the above two facts:

$$z_c(k_F,0;k)\simeq(4\sqrt{3}/k_{\rm FT})\exp(-2\sqrt{3}k/k_{\rm FT})\ . \tag{2.25}$$

The first try turned out to fit z_c reasonably well as a function of density as illustrated in Fig. 2. For $0.75\lesssim k/2k_F\lesssim 0.95$ it does not provide a good-percentage fit to z_c alone, but this does not matter since z_c is so small here that z is dominated by z_x, which takes on its largest magnitudes in this region. It also does not reproduce any of the structure near $k\sim 2k_F$. Since this structure only produces a small change in the total area giving z_c, this feature is actually an improvement over the approximation (2.19): We only *effectively* use (2.25) for $k<k_c<q$ (and for the total area which it predicts correctly); if k is as large as $2k_F$, then $q\gtrsim 2k_F$, so that the structure at $2k_F$ in the true $z(k_F,q;k)$ is so broad that it is effectively nonexistent. Thus our parametrization (2.25) probably rectifies the problems with the original approximation (2.19) in the region $k\sim 2k_F$. In Figs. 2(a)–2(c) the upper curves marked "integral" show the area under the z curves. It is clear that if we use them from the small k end, no appreciable errors will be introduced. Therefore, we write the integral of (2.9) as

$$Z_c(k_F,q)=Z_c(k_F,0)-\int_0^{k_c} z_c(k_F,0;k)dk\ , \tag{2.26}$$

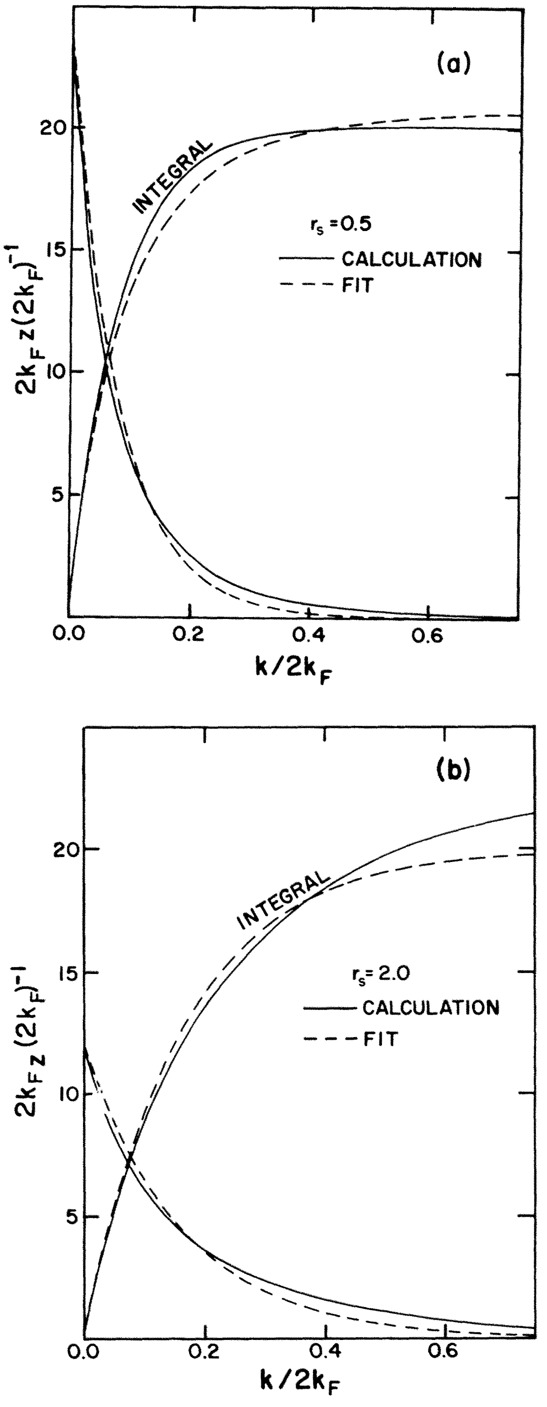

FIG. 2. Contribution Z_c to the nonlocal exchange-correlation energy for $q=0$ for (a) $r_s=0.5$ and (b) $r_s=2.0$. The solid curves represent the RPA calculation of I, while the broken curves are the fit (2.27). The curves marked "integral" are the areas under the respective z curves multiplied by 10 and may be used to obtain the error in the integral in (2.26) due to the fitting procedure.

and take $Z_c(k_F,0)\simeq 2$ and use (2.25) for $z_c(k_F,0;k)$, and find

$$Z_c(k_F,q)=2\exp(-2\sqrt{3}k_c/k_{FT}) , \qquad (2.27)$$

where the q dependence occurs only through k_c. The total Z is given according to (2.23) by

$$Z(k_F,q)=Z_c(k_F,q)-\tfrac{7}{9} . \qquad (2.28)$$

Then according to (2.7) and (2.9) the nonlocal (NL) part of $E_{\rm xc}$ is given by

$$E_{\rm xc}^{\rm NL}=\frac{e^2}{4\pi^3}\int d^3r\,[k_F(\vec{r})]^2[q(\vec{r})]^2 Z(k_F(\vec{r}),q(\vec{r})) . \qquad (2.29)$$

Using (2.27), (2.28), and (2.5) gives

$$E_{\rm xc}^{\rm NL}=\frac{e^2}{16\pi^3}\int d^3r[\vec{\nabla}k_F(\vec{r})]^2 \times\left[2\exp\left[-\frac{2\sqrt{3}k_c}{k_{\rm FT}}\right]-\frac{7}{9}\right] . \qquad (2.30)$$

Finally, using (2.20) and restoring n as a variable instead of k_F, we find [Eq. (12) of LM]

$$E^{\rm xc}=(E_{\rm LDA}^{\rm RPA})^{\rm xc}+a\int d^3r\frac{[\vec{\nabla}n(\vec{r})]^2}{[n(\vec{r})]^{4/3}}(2e^{-F}-\tfrac{7}{9}) , \qquad (2.31)$$

where

$$F=b\,|\vec{\nabla}n(\vec{r})|/[n(\vec{r})]^{7/6} . \qquad (2.32)$$

Taking rydbergs and bohrs to be the units of energy and length, respectively, the constants a and b are given by

$$a=\pi/[8(3\pi^2)^{4/3}]=4.287\times 10^{-3} , \qquad (2.33)$$

$$b=(9\pi)^{1/6}f=1.745f=0.2618 , \qquad (2.34)$$

where the final equality incorporates the value $f=0.15$. The quantity $(E_{\rm LDA}^{\rm RPA})^{\rm xc}$ is the local-density approximation for $E^{\rm xc}$ *in the random-phase approximation* (RPA), for which we have found in all applications reported here that the von Barth–Hedin[34] parametrization is adequate. We emphasize that since the nonlocal part is based on the RPA, it is not consistent to use any other approximation than the RPA for the local part; otherwise, the large cancellation between these terms will be partially lost. We have discussed this point previously, and will again later in a planned future paper.

To apply (2.31) to real systems one would generally use the Kohn-Sham[2] method for which we need the functional derivative

$$v^{\rm xc}(\vec{r})=\delta E^{\rm xc}/\delta n(\vec{r}) .$$

This is straightforwardly worked out, and one finds [Eq. (13) of LM]

$$v^{\mathrm{xc}}(\vec{\mathrm{r}})=(v_{\mathrm{LDA}}^{\mathrm{RPA}})^{\mathrm{xc}}(\vec{\mathrm{r}})+2an^{-1/3}\left\{\frac{7}{9}\left[\frac{\vec{\nabla}\cdot\vec{\mathrm{K}}}{n}-\frac{2K^2}{3n^2}\right]-2e^{-F}\left[\frac{(1-F/2)\vec{\nabla}\cdot\vec{\mathrm{K}}}{n}-\left[\frac{2}{3}-\frac{11F}{6}+\frac{7F^2}{12}\right]\frac{K^2}{n^2}+\frac{F(F-3)\vec{\mathrm{K}}\cdot\vec{\nabla}\,|\vec{\mathrm{K}}|}{2n\,|\vec{\mathrm{K}}|}\right]\right\}, \tag{2.35}$$

where $\vec{\mathrm{K}}=\vec{\nabla}n(\vec{\mathrm{r}})$.

We now estimate the sizes of various terms. Consider the example of the Be atom discussed earlier at the 1s radius (~ 0.4 bohr); one has

$$F \simeq 0.26(11/1.5)(1.5)^{-1/6}=1.8 .$$

This gives $e^{-F}=0.17$. Therefore, $Z_c=2\times 0.17=0.34$ and $Z_x=-0.78$, leading to $Z=-0.44$. Note that the nonlocal correlation energy has been reduced by more than a factor of 5 so that the negative nonlocal exchange is dominant. The quantity $|Z\delta|$ [see (2.18)] gives an even closer estimate of the error in the LDA than is present in δ alone: $|Z\delta| \sim (0.12)(0.44) \sim 5\%$, which is very close to the actual error of 6%. We also can repeat the above estimate for $r \sim 2.6$ bohr corresponding to the 2s orbital. In this case $n \sim 0.008$, $|\vec{\nabla}n(\vec{\mathrm{r}})/n(\vec{\mathrm{r}})| \sim 1.2$ giving $\delta=9\%$, or a value not much different in fractional terms from that for the 1s orbital. However, from (2.20) we get $F=0.72$, so that $Z_c \sim 0.98$, $Z_x \sim -0.78$, and so that $Z \sim +0.20$. Therefore, in this case nonlocal *correlation* dominates nonlocal exchange, as might be expected.

One would certainly expect from inspecting Fig. 1(a) that our most basic approximation $q \ll k_F$ breaks down completely when $q=2k_F$. This occurs only in the extreme low-density tails of atoms, molecules, or surfaces. For atoms one has $|\vec{\nabla}n(\vec{\mathrm{r}})/n(\vec{\mathrm{r}})| \sim 1$, or somewhat greater in the tail, so that $q=2k_F$ corresponds to a density $n \sim 10^{-5}$, or somewhat greater. This occurs a long way out in the tail and has no noticeable effect on the energies, densities, or potentials in the bulk of an atom. However, out in the tail v^{xc} [Eq. (2.35)] is affected, and after beginning to increase, as required to simulate the fact that the attractive force is too weak at large distances in the LDA, it continues to increase instead of approaching a constant. Although this asymptotic failure has virtually no effect on anything we would want to calculate, it is troublesome numerically, and we chose to cut it off following the method of Herman *et al.*,[35] who applied empirical potentials of forms similar to (2.35) to atoms. Hence in all the self-consistent calculations reported here both the nonlocal contribution to v^{xc} [Eq. (2.35)] and the nonlocal contribution to E^{xc} [Eq. (2.31)] were multiplied by

$$\exp\{-h[\vec{\nabla}n(\vec{\mathrm{r}})/n(\vec{\mathrm{r}})]^2[n(\vec{\mathrm{r}})]^{-2/3}\} ,$$

where $h=10^{-4}$. This value of h is 1–2 orders of magnitude smaller than those typically used by Herman *et al.*,[35] so that our cutoff occurs at a larger distance. It was found that starting from this value h could normally be changed by an order of magnitude without affecting the results for energies, eigenvalues, and densities at reasonable distances. Just as for the potential of Herman *et al.*, if the external potential is singular, introducing cusps in the density as occur near atomic nuclei, then these cusps cause a very weak singularity whose form is to change the $1/r$ divergence of the "nuclear" Coulomb potential by $\sim 1\%$. The fact that v^{xc} is large and negative is a real physical effect, as the electronic densities near atomic nuclei are too low in the LDA. Of course, the persistence of this v^{xc} to remain a constant fraction of the nuclear potential all the way to the nucleus is spurious and is a result of the failure of the single-q approximation with q represented by (2.5). Fortunately, the effect of this inaccuracy seems almost imperceptible both because it is so weak and because the fraction of the electron number in the spurious potential region is small.

Finally, we conclude this section by a more accurate estimate for the validity of the gradient expansion than was possible hitherto. This is easily done, since the gradient approximation is nearly exactly given by (2.31) with $F=0$. The fractional correction to the gradient approximation is, therefore, $(1-e^{-F})\frac{18}{11}$, which could be replaced by $\frac{18}{11}F$ if this is to be much less than 1. This may be written alternatively using (2.33), (2.27), and (2.5) as (assuming $f \sim \frac{1}{6}$)

$$\frac{0.43\,|\vec{\nabla}n(\vec{\mathrm{r}})|}{[n(\vec{\mathrm{r}})]^{7/6}} \simeq \frac{6q(\vec{\mathrm{r}})}{k_{\mathrm{FT}}(\vec{\mathrm{r}})} \simeq \frac{|\vec{\nabla}n(\vec{\mathrm{r}})|}{k_{\mathrm{FT}}(\vec{\mathrm{r}})n(\vec{\mathrm{r}})} \ll 1 , \tag{2.36}$$

where the leftmost equality assumes atomic units. The simple gradient expansion is expected to be valid when the inequality in (2.36) is satisfied. In terms of q (or k_c) this is what was derived in Appendix C of I, that is, the middle equality in (2.36) was obtained correctly from the explicit calculation there. On the other hand, q was overestimated to be $\sim |\vec{\nabla}n(\vec{\mathrm{r}})|/n(\vec{\mathrm{r}})$, while our present estimate which has been verified by trials in many systems gives

$$q(\vec{r})\sim f[\,|\vec{\nabla}n(\vec{r})|/n(\vec{r})]\sim|\vec{\nabla}n(\vec{r})|/6n(\vec{r})\ .$$

Therefore, the first and third quantities on the left of the inequality in (2.36) differ from I, being less severe by a factor of 6. (In LM the criteria $k_{FT}\xi\gg 36$ is also too severe by a factor of 6.) We note also that the criterion (2.18) for the LDA is good.

$$\delta\simeq\frac{q^2}{k_F^2}\simeq\left[\frac{\vec{\nabla}n(\vec{r})}{k_F(\vec{r})n(\vec{r})}\right]^2\ll 1 \tag{2.37}$$

is also less severe than we had previously supposed, so that the situation where (2.37) is well satisfied and (2.36) is badly violated is still a most prevalent one. For example evaluating (2.36) at the 1*s* radius in Be gives $|\vec{\nabla}n(\vec{r})/k_{FT}(\vec{r})n(\vec{r})|\sim 2.5$, while as before (2.37) gives $\delta\sim 0.12$. Similarly, evaluating (2.36) at the 2*s* radius in Be gives $|\vec{\nabla}n(\vec{r})/k_{FT}(\vec{r})n(\vec{r})|\sim 1.2$, while as before (2.36) gives 0.09.

Unfortunately, we are unable to derive the precise criteria for our new expression (2.31) to be valid. It was designed to get around the poorly satisfied criterion (2.36) and this it does do. Given that a single q is reasonable or effectively so, then we believe the *basic physics* of our approximation to be valid when $q\ll 2k_F$, which is a criterion similar to (2.37). However, in addition we have made the additional approximation of replacing a smooth cutoff with a sharp one and using the gradient expansion all the way down to the cutoff, and we know of no way of quantifying the error in this procedure *a priori* in the absence of a calculation of the exact curve over the whole range for realistic physical situations. On the other hand, we will access the error *a posteriori* in the tests in the following sections, and we defer the remainder of this discussion until then.

III. APPLICATIONS OF THE METHOD

A. Ground-state energies of atoms

Here we compare self-consistent nonrelativistic calculations using (2.21) and (2.25) with the "exact" nonrelativistic results for the spinless atoms through argon. The "exact" results were determined by the same method used recently by Perdew and Zunger[17] based on the work of Veillard and Clementi[36] and consisted of subtracting the Hartree-Fock relativistic correction[37] from the experimental ionization potential sum,[38] with no attempt to make quantum-electrodynamic (QED) corrections. The error in the ordinary relativistic correction may be estimated by comparing the results of Ref. 37 with full Dirac-Fock calculations,[38] while Ref. 37 lists values for the latter correction. In any case the error is less than 0.01 Ry, except for Mg and Ar where we estimate the respective errors as ±0.02 and ±0.1 Ry. Even these are unimportant for the comparisons made in this section, but later on when we consider a more accurate functional, these errors become significant. Of course the "exact" results obtained in this way also agree with numerical (multiparameter variational and configuration interaction) calculations for the lightest atoms to 0.01 Ry or better. The latter calculations are of course also "exact" by virtue of their size.

Our results are displayed in Table I, which for the most part has already been published,[1] but to less accuracy. As before, we show the results of calculations based on several other local and nonlocal approximations as well. All the local approximations give energies too high (magnitude too low). The values in the row marked "local (Ceperley)" were calculated assuming that the approximate analytic form given in Ceperley's paper[39] to fit his data was valid at all densities. Vosko *et al.*[40] and Perdew and

TABLE I. Atomic ground-state energies in various approximations (Ry).

	He	Be	Ne	Mg	Ar
Local (Ceperly)[a]	−5.67	−28.88	−256.39	−398.17	−1051.70
Local (RPA)[b]	−5.74	−29.03	−256.82	−398.69	−1053.51
Hartree-Fock[c]	−5.72	−29.15	−257.09	−399.23	−1053.64
Present nonlocal ($f=0.15$)	−5.80	−29.21	−257.36	−399.36	−1053.66
Present nonlocal ($f=0.20$)	−5.84	−29.28	−257.54	−399.57	−1053.98
Exact[d]	−5.81	−29.33	−257.84	−400.08	−1055.08
Self-interaction corrected[e]	−5.84	−29.39	−258.55	−401.06	−1056.84

[a] Reference 39.

[b] von Barth—Hedin parametrization, Ref. 34.

[c] Reference 44.

[d] See text.

[e] Reference 17.

Zunger[17] have suggested procedures for matching Ceperley's, or preferably still, Ceperley and Adler's[41] results at small r_s to the exact power-series expansion, but these improvements do not have much affect on the calculations made here, giving only slightly lower energies. Similarly, in the column marked "local (RPA)," we have found in this spin-independent calculation that the von Barth–Hedin[34] parametrization was adequate, and all RPA numbers in this paper have been calculated using this parametrization, and although we have heeded the warning of Vosko *et al.*,[40] it has been found[42] that in this case the error involved is negligible. We have also tried other local approximations[43,18] and find that these are generally bracketed by the given Ceperley and RPA values. Also included in the table are the Hartree-Fock[44] values, which almost always represent an improvement over any local approximation. We have also reproduced the results of the self-interaction-corrected (SIC) calculation of Perdew and Zunger,[17] which generally exaggerates the nonlocal correction, but nevertheless gives values closer to the exact energies than the Hartree-Fock method gives. The energies were calculated by our present nonlocal method both with the value of $f=0.15$ [Eq. (2.34)], which is the value we have adopted for the bulk of our calculations, and for $f=0.20$, for the purposes of comparison. Generally, these calculations represent a substantial improvement over all local approximations, as well as over the Hartree-Fock approximation, and are for the most part even better than the SIC calculations of Perdew and collaborators.[15–17]

We believe that it is highly inappropriate to adjust f to obtain a best fit for a particular calculation, at least if this value differs much from 0.15. Using this latter value, which is physically based both for surfaces and atomic orbitals, we have found substantial improvements in *all* physical systems we have tried it on. Increasing f in order to get, for example, a better fit to the total energy of the neon atom, not only would make the helium results worse, but also begins to distort the predicted densities in the valence shells in an unphysical way; it also makes the results for surface energies worse. We hope to give convincing evidence later in this paper that the main source of error in our nonlocal approximation, at least so far as total energies of atoms goes, has nothing to do with the sharp cutoff [Eq. (2.19)] or the method of determining it [i.e., Eq. (2.20) and the choice of f], but rather with our approximation to the exchange. To try to correct this latter error artificially by adjusting f is not only physically incorrect, but also bound to be unsuccessful, at least when a variety of properties are considered.

B. Removal energies in atoms

Here we summarize our results for the removal energies of outer atomic electrons. The calculations were done by expressing these energies as differences between the ground-state energies of two different systems. Because our approximations here apply only to the case of no spin density, we calculate these energies only for the removal of complete angular momentum shells.

The results of our nonrelativistic calculations are given in Table II. These are essentially the same numbers as contained in LM, except that we have added LDA calculations according to the Ceperley approximation. The Cu^+ and Zn^{2+} results were omitted because of our fear that relativistic effects could influence the results for removing ten electrons from ions this heavy and because the presumed inaccuracies in the experimental results preclude a precise comparison anyway.

As opposed to the case for the ground-state energy, the addition of beyond-RPA corrections improves the removal energies in the LDA, as ap-

TABLE II. Removal energies of outer shells of electrons in atoms (Ry).

Atom	Subshell	Local[a] (Ceperley)	Local[b] (RPA)	Nonlocal[c] (present)	Experiment[d]
He	1*s*	5.67	5.74	5.80	5.81
Be	2*s*	2.00	2.07	2.00	2.02
Mg	3*s*	1.69	1.76	1.66	1.67
Ca	4*s*	1.35	1.41	1.31	1.32
Zn	4*s*	2.08	2.14	2.04	2.01
Ne	2*p*	37.46	37.71	37.44	37.28
Ar	3*p*	22.76	22.99	22.82	22.78

[a] Reference 39.

[b] von Barth–Hedin parametrization, Ref. 34.

[c] $f=0.15$.

[d] Reference 38.

parently first noticed by Vosko *et al.*[40] As will be discussed in a planned future paper, we believe this improvement is due at least partially to a spurious self-interaction effect which is present in the beyond-RPA corrections. In any case our nonlocal functional gives an improvement over either local approximation and also correctly predicts a *positive* correction for He and a *negative* correction for the other elements when referred to the RPA. As for sensitivity to f, we find that increasing f from 0.15 to 0.16 increases the removal energy per electron generally less than 2 or 3 mRy.

C. Surface energies

As mentioned in LM, we have also calculated the exchange-correlation contribution to the surface energies for a planar surface. These were not self-consistent calculations, and we have used the linear potential model[45] with $y_F = 3.5$ to simulate a jellium surface with a bulk $r_s = 2.07$, and $y_F = 2$ for $r_s = 4$. Unfortunately, there exist no exact results with which to compare. We could not use the exact results[46] for the infinite barrier model ($y_F = 0$) because, as y_F becomes small, the criterion which we always assume, $q \ll 2k_F$, is badly violated, as the recent work of Sahni *et al.*[47] clearly shows. Thus we were forced to compare with other approximate calculations, and since the average slope model[5,6] is really an approximation to which one supposes our present cutoff approximation represents an additional approximation, we compare with average slope results. This is shown in Table III, where the sensitivity to f is also indicated. The results are more sensitive to f than our atomic results (except for He) because nonlocal correlation and nonlocal exchange are in this case both large in magnitude and nearly cancelling, so that a small change in the correlation component can make a relatively large fractional change in the total. This is especially true as y_F is decreased.

In any case the value $f = 0.15$ which we have adopted yields qualitatively correct predictions. Note especially that the sign of the nonlocal component is *positive*, while for ground states of atoms it is *negative*, and that our approximation correctly predicts this feature.

D. Densities of heliumlike atomic species and beryllium

The species of the He isoelectronic series are simple enough to be solved as accurately as anyone could conceivably wish by multiparameter variational techniques, for the energy E as well as the electronic density $n(r)$. In this single-orbital case $n(\vec{r})$ can be reasonably characterized by its moments

$$\langle r^m \rangle \equiv \int d^3r\, r^m n(\vec{r})$$

and by its value at the nucleus $n(\vec{0})$. We compare the exact[48] values with our nonlocal approximation and with various other approximations in Tables IV(a), IV(b), and IV(c) for He, Li$^+$, and Be^{2+}. As opposed to the energy, the densities show virtually no sensitivity to which a local approximation is used; the values in the table were calculated with the von Barth–Hedin[34] parametrization. Nor are the nonlocal values very sensitive to f. The ones shown were calculated with $f = 0.15$.

We see that the present nonlocal method gives substantial improvements over the LDA in every case tried, although for most cases our results are not superior to the Hartree-Fock results, especially as the ionization state increases and the Hartree-Fock method becomes more nearly exact.

The case of the beryllium atom is more interesting because it has both valence and core electrons. The configuration-interaction calculations[49] for the density seem fairly well converged for the density in this atom and we take them to be exact.

In Fig. 3 we compare our results for the radial density $4\pi r^2 n(r)$ in various approximations with the exact results. Since the LDA gives densities which are quite close to the exact ones, we always plot the difference between the density in a given approximation with that of the LDA with the von Barth–Hedin parametrization of the RPA.

First consider the Hartree-Fock (HF) approximation as a nonlocal correction to the LDA. In the tightly bound region of the 1s orbital where exchange dominates correlation we expect *a priori* the HF approximation to be valid and the figure confirms this. Similarly, in the region between the orbitals the density is lowered due to exchange repulsion; the figure shows that the HF approximation

TABLE III. The nonlocal exchange-correlation component of surface energies in various approximation (ergs/cm^2).

r_s	Average[a] slope	Present $f = 0.12$	Present $f = 0.15$	Present $f = 0.17$
2.07	117	140	85	57
4.00	22	28	19	14

[a] References 5 and 6.

TABLE IV. Density moments (a.u.) for (a) He, in (b) Li^+, and (c) Be^{2+} in various approximations, and ground-state energy (Ry). $n(\vec{0})$ is the density at the origin, and $\langle r^m \rangle \equiv \int d^3r\, n(\vec{r}) r^m$.

	Local	HF	Present	Exact
		(a)		
$n(\vec{0})$	3.53	3.60	3.61	3.62
$\langle r^{-2} \rangle$	11.7	12.0	11.9	12.0
$\langle r^{-1} \rangle$	3.31	3.37	3.35	3.38
$\langle r \rangle$	1.92	1.85	1.88	1.86
$\langle r^2 \rangle$	2.56	2.37	2.44	2.39
$-E$	5.67	5.73	5.80	5.81
		(b)		
$n(\vec{0})$	13.43	13.67	13.68	13.70
$\langle r^{-2} \rangle$	29.3	29.8	29.7	29.9
$\langle r^{-1} \rangle$	5.30	5.38	5.35	5.38
$\langle r \rangle$	1.169	1.145	1.155	1.146
$\langle r^2 \rangle$	0.936	0.891	0.909	0.893
$-E$	14.36	14.47	14.51	14.56
		(c)		
$n(\vec{0})$	33.9	34.4	34.4	34.4
$\langle r^{-2} \rangle$	54.8	55.7	55.5	55.7
$\langle r^{-1} \rangle$	7.30	7.37	7.35	7.38
$\langle r \rangle$	0.842	0.828	0.834	0.829
$\langle r^2 \rangle$	0.481	0.464	0.471	0.464
$-E$	26.96	27.22	27.21	27.31

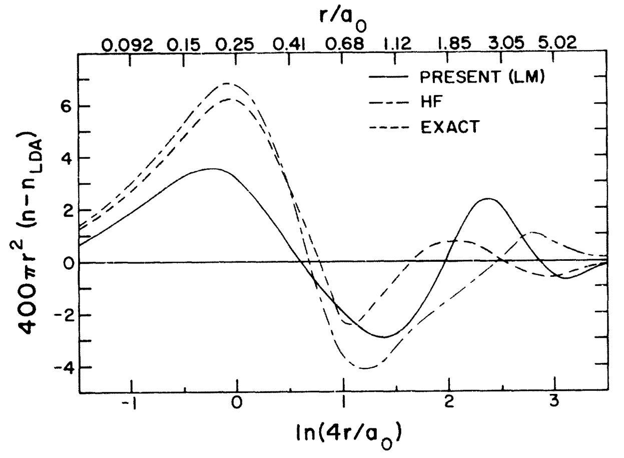

FIG. 3. Radial density different (×100) between the prediction of a given theory and the local-density approximation (in RPA). The solid curve is the present approximation calculated from Eq. (2.35), while the broken line is the Hartree-Fock approximation. The "exchange-only" densities of Sec. IV are virtually indistinguishable from the Hartree-Fock ones. The dashed line labeled "exact" is the configuration interaction calculation of Ref. 49.

exaggerates this; in reality, this effect is partially screened out as a result of correlation. Finally, in the region of the 2*s* state, where correlation is important, one sees that the HF approximation is much worse than the LDA and even gets the sign of the correction wrong through most of this region.

Now turning to our present nonlocal correction we see that it correctly predicts a depletion in density between the orbitals, and this depletion is correctly predicted to be weaker than that of the HF approximation, although displaced to slightly larger radius than it should be. The electrons from this depleted region must appear in the 1*s* or 2*s* regions, and the present scheme, although correctly predicting a rise in both regions, slightly miscalculates the balance, with too small an increase in the 1*s* region and too large an increase in the 2*s* region. Nevertheless, all the qualitative corrections to the LDA are given correctly, including the sign of the correction in the outer region which the HF approximation gets wrong. We argue, therefore, that the present functional does include most of the important physics.

For comparison, we show in Fig. 4 the density difference between a given approximation and the RPA in the local-density approximation, using various commonly used correlation-energy expressions. Notice that all of these give only very small corrections to the density, much smaller than our nonlocal theory and much smaller than needed. Notice also that they all predict a correction in the *wrong direction.* This latter fact may be a true prediction within the LDA, that is, beyond-RPA effects within the LDA may indeed make the density worse. On the other hand, one cannot entirely rule out the hypothesis that the electron-gas calculations incorrectly predict the *density dependence* of the correlation energy in the density region crucial to these calculations. In any case it should be absolutely clear that no local approximation can give the correct atomic densities.

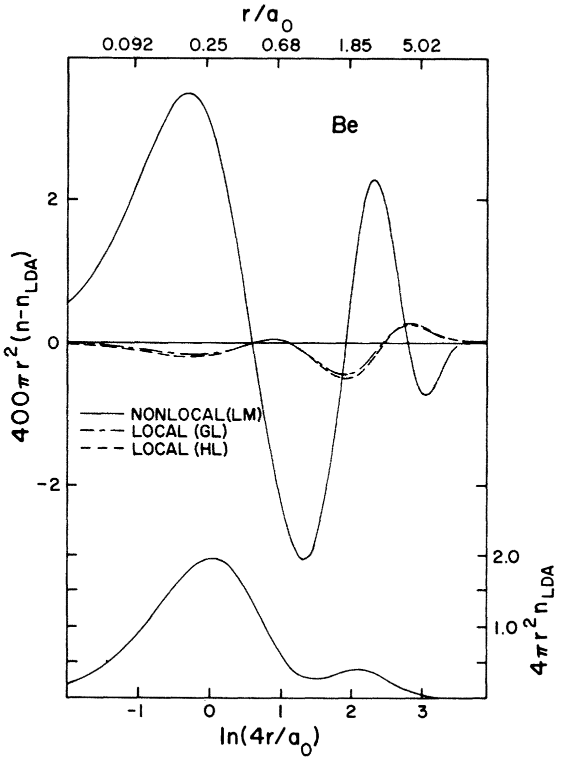

FIG. 4. Radial densities in Be implied by local vs nonlocal approximations. The solid curve is our nonlocal approximation as shown in Fig. 3. As before, all curves are subtracted from the value in the von Barth–Hedin (Ref. 34) parmetrizations of the RPA in the LDA, which is plotted using the right vertical scale at the bottom of the figure. The broken line represents the LDA in the Gunnarsson-Lundqvist approximation (Ref. 18) while the dashed line is the Hedin-Lundqvist approximation (Ref. 43).

E. Eigenvalues

The eigenvalues of the Kohn-Sham Schrödinger equations, except in certain special cases, do not have a known physical meaning. It is also clear that the *difference* (i.e., subtract one from another) between these eigenvalues must be given very accurately by the LDA, and still more accurately by our nonlocal correction, relative to the eigenvalues of the exact Kohn-Sham potential. This follows because the LDA densities are close to the exact ones and our nonlocal ones are much closer. Thus the exact Kohn-Sham potential could differ substantially from ours only by a constant additive term or in a region where the density is virtually zero (large r), or a combination of the two. The above changes in the potential affect only the *absolute level* of the eigenvalues and not the *differences* between them. The above conclusion was first obtained by Perdew and Norman[24] by a different argument: They made a direct comparison of the eigenvalues in the LDA for exchange only with the *exact* Kohn-Sham eigenvalues for exchange only.

Therefore, it is not surprising that the corrections to the LDA eigenvalue differences which we find are small. For example, for Be we find (nonlocal) $|\epsilon_{2s}-\epsilon_{1s}|=7.34$ Ry, while in LDA (RPA) this difference is 7.30 Ry. On the other hand, the *highest* eigenvalue (for an atom) in an exact Kohn-Sham theory presumably does have direct physical meaning since it controls the asymptotic density, and should be at least an approximation to a removal energy.[17] On the other hand, the top LDA eigenvalues are not equal to approximate ionization energies, and our nonlocal correction does not improve the situation. This is probably because our assumption $q \ll k_F$ fails drastically as the density vanishes at large r, as discussed earlier. The exact Kohn-Sham potential is probably similar to ours but is shifted by a constant over the region where the density has a non-negligible magnitude and varies as $-e^2/r$ way outside this region. For reference, in Be the $2s$ eigenvalue has a magnitude -0.44 Ry in the LDA (RPA) and -0.43 Ry in our nonlocal approximation, while the experimental ionization energy is 0.69 Ry.

F. The potential

The properties of our self-consistent exchange-correlation potential are discussed here. In Fig. 5 we show for Be the difference between the self-consistent potentials for our nonlocal scheme ($f=0.15$) and the LDA multiplied by the radius r. We denote this by $r\delta v_{xc}$. Thus the plot gives some idea of the fractional change in potential associated with nonlocal effects.

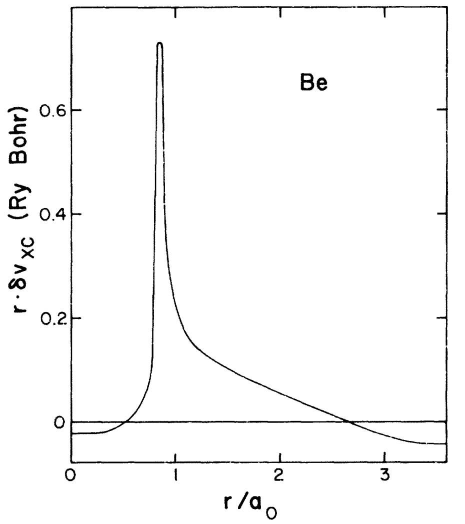

FIG. 5. Difference in the total self-consistent Be potential δv_{xc}, with and without the nonlocal contribution of Eq. (2.35), multiplied by r.

Before discussing the large peak, we mention some less prominent features in $r\delta v_{\mathrm{xc}}$. First, it becomes negative for small r. This is correct because the LDA has too low a density in this region and more electrons need to be pulled in. On the other hand, the intercept at $r=0$ should rigorously be zero; the fact that the above negativity persists all the way to $r=0$ (i.e., a finite intercept) is a flaw (but a numerically almost negligible flaw) in our method which we have discussed earlier. At large r the curve rises slowly; this happens off the r scale of Fig. 4, but may be seen in Fig. 5. This tightens the density at large r as required. However, the rise becomes more rapid as the density vanishes; this represents a breakdown of our assumption $q \ll k_F$ as discussed earlier.

The most prominent feature is the large positive peak near $r \sim 1$ a.u. This is at the interface region between where the density is dominated by 1s states and where it is dominated by 2s states. Such peaks in v_{xc} occurring between shells were evident (although greatly exaggerated) in the earlier work of Herman *et al.*[35] who used an empirical v_{xc} of a type similar to (2.35); more importantly such peaks are also evident in the work of Talman and collaborators,[21,23] who provide an exact implementation of what we like to call "exchange only"; these peaks are also evident in the preliminary results of von Barth,[25] who has provided an exact calculation of the Kohn-Sham v_{xc} corresponding to the Hartree-Fock approximation. A discussion of these calculations is most appropriately postponed until the next section. The important point here is that the peak is a real exchange effect. In the Hartree-Fock–type schemes one uses a nonlocal potential, or alternately and equivalently, a different local potential for each orbital. In the Kohn-Sham scheme, an equally valid formulation of the problem, the effect of the nonlocal potential of the former scheme is produced by a spike *between* each of the orbitals. In our case the spike presumably represents the "exchange repulsion" (screened in this case by correlation effects) between electrons of like spin. It is this spike that causes the depletion in density in the interorbital region discussed in the last subsection.

In Fig. 6 we show the exchange-correlation potential Be as computed in the LDA and our nonlocal approximation [Eq. (2.35)], as well as the *exact* results for *exchange only* which we calculated from the data given in Ref. 23. The prominent feature of the two nonlocal results is the peak which occurs at the same position and has roughly the same strength and shape both for our approximation and for exact exchange. This gives clear and unambiguous confirmation to our conjecture earlier in this section that the peak was a true exchange effect. It also provides striking evidence that our nonlocal functional is giving a good approximation to physical reality.

In fact, the largest difference between our v_{xc} and the exact one for exchange only would be removed if a constant of ~ 0.2 Ry were subtracted from our potential. This is just about the difference in highest eigenvalues between the two approximations. As

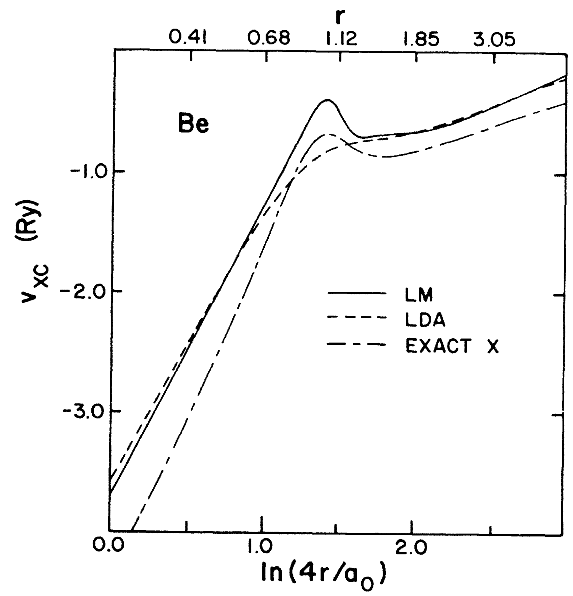

FIG. 6. Total self-consistent exchange-correlation potential in Be in the cusplike region. The solid curve is our approximation of Eq. (2.35), the dashed curve is the local-density approximation (Ref. 34) while the broken curve represents the "exchange-only" calculation, using the potential of Ref. 23.

discussed earlier, our potential is in error by an additive constant in the region where the density is nonvanishing (and by an undetermined nonconstant amount in the very-large-r region where the density is, for all practical purposes, zero). Correcting the constant error of course has no affect on any calculated property except the level of all eigenvalues. The nonconstant error in the region of asymptotically vanishing density affects only the calculation of this asymptotically vanishing density; it affects only negligibly the calculated density in other regions, the total energy, and the eigenvalues of occupied states.

G. Application to solids

We have not attempted to apply our method to solids (except for our jellium surface case). However, our success with atoms suggests that the use of our functional would substantially improve the LDA results for ground-state properties of solids such as cohesive energy, lattice constant, and elastic constants. Indeed preliminary calculations by von Barth *et al.*[50] show substantial improvements for the above quantities in crystalline bulk silicon.

It has been argued[51] that the eigenvalues of the *exact* Kohn-Sham potential should give the minimum (possibly indirect) gap correctly in semiconductors. The LDA calculation of this gap is often in serious error. Will our nonlocal potential improve the situation? The problem, in principle, with this sort of application is that our method only gives correctly the eigenvalue differences for *occupied* states; there is no guarantee that the difference in eigenvalue between an unoccupied state and an occupied state be given correctly (i.e., equal to what the exact Kohn-Sham potential would give) because our potential is in error in regions of very low density, and the unoccupied states of interest may well have non-negligible components in these regions (the LDA has the same defect). Therefore, a traditional-style calculation of semiconductor bandstructure using our scheme may well fail to show any improvement over the LDA; indeed, this is what is indicated by the preliminary result of von Barth *et al.*[50] for silicon.

A possible solution to this defect in our scheme would be to do the calculation with the states above the gap occupied. This would presumably remove the error in our potential for all states which determine the gap. On the other hand, it would no longer be a calculation of a pure semiconductor, but rather one "highly doped" with a uniform positive background of charge. Whether this fictitious system with a good exchange-correlation potential has a gap more representative of a real semiconductor than the real semiconductor with a bad exchange-correlation potential is a question which we cannot answer, but by varying the "doping" one could probably get a good indication.

IV. EXCHANGE AND CORRELATION SEPARATELY

A. Motivation and definitions

The reason for attempting to separate exchange and correlation is, of course, that the latter may be calculated exactly, although often not trivially, in many cases. Applications of this sort to atoms have been made for example by Wilk,[52] and more recently by von Barth[25] using the functional of the present paper.

There are two obvious ways to *define* what one means by the inclusion only of exchange and the exclusion of correlation, which coincide in the case of a uniform system. Since their difference has led to confusion in the past, we will discuss them carefully. Consider a system of N electrons with a nondegenerate ground state and density $n_g(\vec{r})$: $N=\int d^3r\, n_g(\vec{r})$. We might generate an approximation to this density, $n(\vec{r})$, from the ground state of a noninteracting system with a local potential $v_L(r)$, that is,

$$n(\vec{r})=\langle \psi_L \mid n^{\text{op}}(\vec{r}) \mid \psi_L \rangle \ , \tag{4.1}$$

where $\mid \psi_L \rangle$ is the ground state (assumed nondegenerate) of

$$H_L \equiv \sum_{i=1}^{N} [P_i^2/2m + v_L(\vec{r}_i)] \ . \tag{4.2}$$

We assume $n(\vec{r})$ to be such that this is possible. In the cases considered here of surfaces and closed-shell atoms, the problem raised by Lieb[53] and by Levy[54] never arises. By the exchange energy for the density $n(\vec{r})$ here we mean

$$E_x=\langle \psi_L \mid V \mid \psi_L \rangle - E_{\text{Coul}} \ , \tag{4.3}$$

where E_{Coul} is the Coulomb energy

$$E_{\text{Coul}}=\frac{e^2}{2}\int d^3r\, d^3r' \frac{n(\vec{r})n(\vec{r}\,')}{|r-r'|} \ ,$$

and

$$V=\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}} \frac{e^2}{r_{ij}} \ . \tag{4.4}$$

Note that our definition (4.3) differs from the usual one, because $\mid \psi_L \rangle$ is not a HF eigenfunction. If v_L is chosen properly, then $n(r)=n_g(r)$. For the Hamiltonian of the problem to be solved,

$$H=\sum_i [P_i^2/2m + v(r_i)] + V \ , \tag{4.5}$$

one minimizes $\langle \psi_L \mid H \mid \psi_L \rangle$ according to Hohenberg and Kohn,[55] with respect to $v_L(r)$ [or with respect to $n(r)$, which is the same thing]. Requiring $\langle \psi_L | H | \psi_L \rangle$ to be a local extremum leads to the set of equations derived by Talman and Shadwick,[21] which are equivalent to solving the Kohn-Sham equations with

$$v_{xc}(\vec{r}) = v_x(\vec{r}) = \delta E_x / \delta n(\vec{r}) , \qquad (4.6)$$

where E_x is given by (4.3). This gives what we call the "exchange-only" approximation, and we label the approximate value of ground-state total energy E_g obtained this way as E_{gx} and the approximate ground-state density $n_g(\vec{r})$ [corresponding to $v_L = v_x$ according to (4.6)] as $n_{gx}(\vec{r})$.

We emphasize that this is *not* the Hartree-Fock (HF) approximation, and E_x is not, in principle, equal to the conventional exchange energy of HF theory. However, at least for atoms the differences are *very* small indeed. This was pointed out by the original developers[21–23] of the method, and more recently by Sahni, Gruenebaum, and Perdew[47,56] who were apparently among the first to recognize the importance of the earlier work[21–23] as a density-functional realization of exchange. In addition, we have calculated the density of the Be atom, which we study extensively in this paper, using the data of Ref. 23; we found it to be virtually indistinguishable from the HF density, at least in plots on the scale of Fig. 3. The ground-state energy is also identical to ±0.01 Ry.

The second obvious method for defining what one means by exchange is the more conventional or Hartree-Fock method. In referring to it we will use the subscript F for Fock instead of the subscript x for exchange. This approximation is defined similarly, except the local potential $v_L(\vec{r})$ is replaced by a nonlocal potential $v_{\rm NL}(\vec{r})$ in Eq. (4.2) so that $| \psi_L \rangle$ is replaced by $| \psi_{\rm NL} \rangle$, the ground state corresponding to a nonlocal potential. However, the fact that $n(r)$ is given by the analog of (4.1) is now not sufficient to define $v_{\rm NL}$, as presumably many such potentials give a particular density. For the ground state the ambiguity is resolved in the usual way, by minimizing $\langle \psi_{\rm NL} | H | \psi_{\rm NL} \rangle$ [see Eq. (4.5)], thus defining $v_{\rm NL}$, the ground-state energy E_{gF}, and the ground-state density $n_{gF}(\vec{r})$. To make a density-functional theory, one needs (in principle) to alter the ground-state densities. One would presumably do this by using a value of $v(\vec{r})$ in (4.5), which no longer corresponds to the physical problem to be solved, but which has the desired $n(\vec{r})$ corresponding to its HF ground state. Then $| \psi_{\rm NL} \rangle$ and $v_{\rm NL}$ would be known and the exchange energy would be defined as a functional of density, analogously to (4.3) as

$$E_F = \langle \psi_{\rm NL} | V | \psi_{\rm NL} \rangle - E_{\rm Coul} + \left\langle \psi_{\rm NL} \middle| \sum_i P_i^2/2m \middle| \psi_{\rm NL} \right\rangle - \left\langle \psi_L \middle| \sum_i P_i^2/2m \middle| \psi_L \right\rangle . \qquad (4.7)$$

The Kohn-Sham potential is thus given by

$$v_{xc}(\vec{r}) = v_F(\vec{r}) = \delta E_F / \delta n(\vec{r}) . \qquad (4.8)$$

Of course, taking

$$v_L(\vec{r}) = v(\vec{r}) + v_{\rm Coul}(\vec{r}) + v_F(\vec{r})$$

in (4.2) gives a $| \psi_L \rangle$ which is *not* the conventional HF wave function, but which gives E_F (not E_x) when substituted into (4.3) and also gives the Hartree-Fock density exactly. A density-functional implementation of the Hartree-Fock approximation has recently been developed by von Barth.[50]

In making a separation between exchange and correlation, one must decide which of the above definitions to use. In a variational sense the Hartree-Fock definition gives slightly better energies than the definition we described first and will call "exchange only." Using a nonlocal potential allows more variational freedom, giving lower total energies and presumably better densities. However, we have seen that this difference is very, very slight, and indeed much smaller than the scale of differences between HF approximations, various local and nonlocal approximations, and the exact results.

Of course, the exchange energy E_x (exchange only) is a simpler quantity than the Fock energy E_F (Hartree-Fock). As pointed out in Ref. (47) the former contains only terms of order e^2, because the $| \psi_L \rangle$'s of (4.3) for a given $n(r)$ are functions only of that $n(r)$ through (4.1) and (4.2), with the single factor of e^2 coming through V [Eq. (4.4)]. However, in order to determine for HF exchange which of the many possible $v_{\rm NL}$'s that give the density $n(r)$ one should use, a separate minimization must be done for each $n(\vec{r})$, so that $| \psi_{\rm NL} \rangle$ is explicitly dependent on e^2. Therefore, E_F [Eq. (4.7)] has terms to all orders in the electron-electron interaction.

What is worse from our point of view, however, is that the gradient series for the Fock exchange term, Eq. (4.7), does not exist,[57] that is to say, it has small-k divergences, and though these are canceled by corresponding terms of the same order in e^2 when correlation is taken into account, it would cause additional problems for us to make an exchange-correlation separation based on Fock exchange. The second-order gradient coefficient for "exchange only" [Eq. (4.3)] not only exists but is given exactly by Sham's original calculation.[32] This is in effect proved in I, where the wave-vector analysis of this coefficient was derived under the assumption that the exchange potential v_x was local.

The relationship of this coefficient to the work of Talman *et al.*[21–23] was apparently first realized by Sahni, Gruenebaum, and Perdew.[47] In the present paper the term exchange will always mean the approximation based on Eqs. (4.1)–(4.6), and *not* on Hartree-Fock exchange. Similarly, correlation energy will refer to the difference $E_{\mathrm{xc}}-E_x$. This will not prevent us from making numerical comparisons with calculations based on HF however, because we know from the previous works of others,[21–23,47] as well as from our own calculations, that the difference between the two approximations is numerically negligible, at least for ground states of the atoms with which we shall deal (although obviously not for larger, nearly uniform systems).

B. Method

The problem with achieving a separation of exchange and correlation is that the local-density approximation, which generally makes a more important contribution to E_{xc} than the nonlocal corrections, does not make this separation accurately. This is most obviously true for atoms from the well-known fact that the LDA often gives a correlation energy which is several hundred percent off, even though E_{xc} is given fairly accurately.

The reason for this inaccurate separation is obvious and well appreciated by many, and stems from the long range of the Coulomb interaction which appears unscreened in either exchange or correlation alone. For our purposes it is best to express the problem in terms of a wave-vector decomposition, which leads us to the behavior of the small-k structure factor S for the uniform system [see (2.6)–(2.8)]. The latter has the rigorous small-k limit[4,33]

$$S(\vec{k})\rightarrow k^2/2m\omega_p \,, \tag{4.9}$$

where ω_p is the plasma frequency. On the other hand, for exchange only (which is the same as HF exchange for a uniform system), one has

$$S_x(k)\rightarrow 3k/4k_F \,. \tag{4.10}$$

The contribution to the exchange energy ΔE_x corresponding to (4.10) is

$$\Delta E_x(k)=\frac{3\pi N_e^2}{2k_F}\frac{1}{k} \,. \tag{4.11}$$

Similarly, since the correlation energy

$$E_c(k)=E_{\mathrm{xc}}(k)-E_x(k) \,,$$

there is a small-k contribution E_c to the correlation energy

$$\Delta E_c(k)=-\frac{3\pi N_e^2}{2k_F}\frac{1}{k} \,, \tag{4.12}$$

so as to cancel (4.11) in the sum E_{xc}. Thus both exchange and correlation energies separately have a large and nonanalytic contribution at small k. They are both real and in fact (4.12) corresponds to the modification of the energy due to the emission and reabsorption of a virtual plasmon; however, this latter effect is rigorously and exactly canceled at small k by the exchange energy (4.11). For a nonuniform system in the LDA these contributions become

$$\Delta E_x(k)=-\Delta E_c(k)=\alpha/k \,, \tag{4.13}$$

where

$$\alpha=\frac{e^2}{2\pi}\int d^3r[k_F(\vec{r})]^2 \,. \tag{4.14}$$

For an infinite system covering all of space the existence of large contributions at small k presents no problem, and if the system has some spacial nonuniformity, then to a good approximation the exchange energy is given by the LDA for exchange energy plus the nonlocal exchange contribution of (2.30) (i.e., set $k_{\mathrm{FT}}=0$, so that only the $-\frac{7}{9}$ term contributes). On the other hand, for a finite system, or a system whose states under consideration are localized within a certain region, of linear size l, it is clear that there must exist a $k_{\mathrm{min}}\sim 1/l$ such that for $k<k_{\mathrm{min}}$ the structure factor is effectively zero, or small. In the LDA for exchange and correlation together the structure factor $S(k)$ is automatically small [Eq. (4.9)]. On the other hand, for exchange only, S_x [Eq. (4.10)] makes a more substantial contribution at small k; it is obvious that any contribution $S_x(k)$ in the form (4.10) for $k<k_{\mathrm{min}}$ is completely spurious. It is also an error that cannot be corrected by any finite-order gradient series. The quantity k_{min} represents a new q (and perhaps a large number of new q's) in the sense of Sec. II. For exchange and correlation together, screening ensures that all lengths longer than the Fermi-Thomas length are irrelevant, but for exchange only this is no longer true, so that the single-q assumption breaks down.

We can correct this error in a crude, zeroth-order manner, but one which we find gives very good numerical results. The approximation we propose is simply to subtract off the spurious contribution coming from the region $k<k_{\mathrm{min}}$, where $S(k)$ is effectively zero, approximating the $S_x(k)$ in the subtraction term by its small-k form of (4.10). Therefore, E_x is replaced by

$$E_x\rightarrow E_x-\int_0^{k_{\mathrm{min}}}\Delta E_x(k)p(k)dk \,, \tag{4.15}$$

which on using (4.13) becomes

$$E_x\rightarrow E_x-\alpha k_{\mathrm{min}}^2/4\pi^2 \,. \tag{4.16}$$

Obviously, the correlation energy must be modified in a complementary way,

$$E_c \rightarrow E_c + \alpha k_{\min}^2 / 4\pi^2 \ . \tag{4.17}$$

The question now is what is $k_{\min}$? It is obviously an extremely nonlocal functional of the density. We speculate that it is a sort of inverse localization length, which is of course different for different types of states in the same system. It would seem obvious that for an infinite system it is zero, at least for regions where the density is dominated by extended free-electron-like states. On the other hand, for single atoms, or for regions in larger systems dominated by single localized atomic orbitals, it is difficult to see how $k_{\min}$ could be much different from the k_c of (2.20) and we will assume that $k_{\min} = k_c$ exactly. Then using (2.20) in (4.16) one gets

$$E_x \rightarrow E_x - 18af^2 \int d^3r [\vec{\nabla} n(\vec{r})]^2 [n(\vec{r})]^{-4/3} \ , \tag{4.18}$$

where a is given by (2.33) and $f \simeq 0.15$. We emphasize that although $k_{\min}$ must be a universal functional of $n(\vec{r})$, the quantity k_c can only be a good measure of it when $\vec{r}$ is sampling a density distribution typical of a localized atomiclike state. If we are correct that $k_{\min}$ is the inverse of some sort of localization or quantization length, then as the states become more extended, $k_{\min}$ becomes smaller than k_c. We do not know how to quantify this, or even for sure that this somewhat speculative idea is correct, but we certainly expect (4.17) to apply to densities in the interior of atoms, whether or not the atom is isolated or part of a solid or molecule, and also to densities that sample the valence electrons in isolated atoms. On the other hand, it is absolutely clear in principle that in the limit of slowly varying densities in an infinite system $k_{\min}$ vanishes in this limit, and vanishes *faster* than k_c so that the correction term in (4.18) does not appear in this limit, and there exist exactly solvable models that demonstrate this unambiguously.[47] It seems equally clear in principle, as we have noted earlier in this section, that a correction such as (4.18) is necessary in the localized limit. We test this numerically later.

Combining (4.18) with the exchange part of (2.31) gives

$$E_x = E_x^{\mathrm{LDA}} - a(\tfrac{7}{9} + 18f^2) \times \int d^3r [\vec{\nabla} n(\vec{r})]^2 [n(\vec{r})]^{-4/3} \tag{4.19}$$

for localized orbitals. Similarly (2.35) for exchange only is to be replaced by

$$v_x(\vec{r}) = v_x^{\mathrm{LDA}}(\vec{r}) + 2a(\tfrac{7}{9} + 18f^2) \left[\frac{\vec{\nabla} \cdot \vec{\mathrm{K}}}{n} - \frac{3K^2}{3n^2} \right] , \tag{4.20}$$

where a is given by (2.33), $\vec{\mathrm{K}} = \vec{\nabla} n(\vec{r})$, and $f \sim 0.15$. Equations (4.19) and (4.20) are analogous to (2.31) and (2.35) for exchange only in atomiclike states.

C. Application to atoms

We have applied Eqs. (4.19) and (4.20) to the self-consistent solution in the spinless atoms through argon. We compare the ground-state energies in Table V with the exact exchange-only numbers of Ref. 23 and other approximations. Notice first that the differences between the LDA for exchange only (first line) have somewhat larger errors when compared with the exact form than the values shown in Table I for exchange and correlation together. This is presumably because of the incorrect division between exchange and correlation that we have been discussing. The second row of Table V represents what we would calculate in a nonlocal approximation if this error were *not* corrected, that is, using (4.19) and (4.20) without the $18f^2$ term. This yields

TABLE V. Atomic ground energies in the "exchange-only" approximation (Ry). The Hartree-Fock values have been appended for comparison.

	He	Be	Ne	Mg	Ar
Local[a]	−5.45	−28.45	−254.98	−396.50	−1049.04
Nonocal[b] ($f=0$)	−5.61	−28.82	−256.01	−397.74	−1051.02
Nonlocal[b] ($f=0.15$)	−5.70	−29.01	−256.54	−398.40	−1052.06
Exact[c] (exchange only)	−5.72	−29.14	−257.09	−399.22	−1053.62
Hartree-Fock[d]	−5.72	−29.15	−257.09	−399.23	−1053.64

[a] $\epsilon_c = 0$ in Eq. (2.3) and $\delta W = 0$ in Eq. (2.2).

[b] Equations (4.19) and (4.20).

[c] Reference 23.

[d] Reference 44.

TABLE VI. Atomic exchange energies in the "exchange-only" approximation (Ry). The Hartree-Fock values have been appended for comparison.

	He	Ne	Ar
Local[a]	−1.71	−21.87	−55.55
Nonlocal[b] ($f=0$)	−1.90	−22.95	−57.50
Nonlocal[b] ($f=0.15$)	−2.01	−23.52	−58.68
Exact[c] (exchange)	−2.05	−24.20	−60.32
Hartree-Fock[d]	−2.05	−24.22	−60.37

[a] $\epsilon_c=0$ in Eq. (2.3) and $W=0$ in Eq. (2.2).
[b] Equations (4.19) and (4.20).
[c] M. Talman *et al.*, cited in Ref. 47.
[d] J. C. Slater and J. H. Wood, Int. J. Quantum Chem. 4, 3 (1971).

errors (row four minus row two) of 0.11, 0.32, 1.08, 1.46, and 2.60 Ry, for the five elements, respectively. This should be compared to errors of 0.01, 0.12, 0.48, 0.72 and 1.42 Ry, respectively, for exchange and correlation together (row six minus row four of Table I). This set of errors should be comparable to the former set if exchange and correlation are being divided properly, since total correlation energy is clearly much smaller than exchange in these systems. Clearly, however, the former numbers are larger than the latter ones by factors of ∼2 or more. This clearly unreasonable result gives evidence that exchange and correlation are still being divided incorrectly. On the other hand, when the full expressions (4.19) and (4.20) are used, the errors corresponding to row four minus row three in Table IV are 0.02, 0.13, 0.63, 0.82 and 1.58 for the five elements, respectively. These correspond very closely with the errors in exchange and correlation together. One would not expect to do much better, because they are undoubtedly produced by inaccuracies in the overall scheme, and not by the divisions between exchange and correlation. We think that the size of this latter set of errors is strong indirect evidence that our division between exchange and correlation is now roughly correct. This view is reinforced by the exchange energies (exchange-only approximation) which are compared with the exact ones in Table VI.

The eigenvalue *differences* calculated from Eq. (4.20) with $f=0.15$ are shown in Table VII where they are compared with the *exact* Kohn-Sham eigenvalue difference for "exchange only," as well as with those calculated for the LDA. As discussed earlier, the LDA gives very good eigenvalue differences, and we see that our correction in every case improves them.

Next, in Fig. 7 we show the deviation in density from the LDA (exchange only) for both this approximation (4.20) and the exact curve which we calculated from the data of Ref. 23. Notice that the improvement of (4.20) over the local approximation is marked, and that the error is also comparable to that in Fig. 3, for exchange and correlation together. Similar trends are observed for neon, whose density moments we show in Table VIII.

TABLE VII. Eigenvalue differences in the "exchange-only" approximation (Ry).

		Local[a]	Nonlocal[b]	Exact[c]
Be	2*s*-1*s*	7.25	7.36	7.64
Ne	2*p*-1*s*	59.58	59.91	59.94
	2*p*-2*s*	1.65	1.68	1.73
Mg	3*s*-1*s*	91.51	91.90	92.15
	3*s*-2*s*	5.41	5.46	5.69
	3*s*-2*p*	3.04	3.05	3.21
Ar	3*p*-1*s*	226.76	227.35	227.72
	3*p*-2*s*	20.79	20.87	21.12
	3*p*-2*p*	16.09	16.10	16.28
	3*p*-3*s*	1.00	1.01	1.01

[a] Local-density approximation for "exchange only."
[b] Equations (4.19) and (4.20) with $f=0.15$.
[c] Reference 23.

TABLE VIII. Density moments for Ne in various "exchange-only" approximations (a.u.).

	Local	Nonlocal[a]	Exact[b]
$n(\vec{0})$	614.2	620.4	619.8
$\langle r^{-2}\rangle$	411.7	414.4	414.8
$\langle r^{-1}\rangle$	30.95	31.05	31.10
$\langle r\rangle$	8.07	8.00	7.90
$\langle r^2\rangle$	10.04	9.78	9.40

[a] Equation (4.20) with $f=0.15$.

[b] Calculated from potential of Ref. 23.

Perhaps the most conclusive test of our method of separating exchange and correlation is the use of (4.19) and (4.20) coupled with (2.31) and (2.35) to calculate the correlation energy of atoms. What we calculate is the "conventional" correlation energy but define for the "exchange-only" definition of exchange, rather than the Hartree-Fock definition (although the difference is small indeed). Thus we solve for the total energy of the atom using the full exchange-correlation functional (2.31)–(2.35), and solve it again using the exchange-only functional of (4.19) and (4.20). For the purposes of this comparison we define the difference between the two results as the correlation energy. Thus we arrange the calculation in a way so that the errors in our approximation for exchange will tend to cancel. Since nonlocal correlation is expected to cancel local correlation, this procedure tends to *magnify* any errors in our method of separating exchange from correlation. The exact correlation energy with which to compare these numbers is simply the difference between the exact ground-state energy, as in row six of Table I, minus the exact ground-state energy in the "exchange-only" approximation, row four of Table V.

We make such a comparison in Table IX. In the first row we use the local-density approximation. In the second row we used our nonlocal form, Eqs. (2.31)–(2.35) with $f=0.15$ for the exchange plus correlation calculation, but we use $f=0$ in (4.19) and (4.20); this incorrectly divides exchange from correlation. In the third row we use the correct division (4.19) and (4.20), with $f=0.15$ for the exchange part of the calculation, with the exchange plus correlation part the same as before. The fourth row is the exact value as discussed earlier. The entries in this table should leave little doubt that we are proceeding correctly.

V. EXACT EXCHANGE PLUS APPROXIMATE NONLOCAL CORRELATION

The preceding section indicates that the largest error in our nonlocal functional (2.31)–(2.35), at least when applied to atoms, comes from the nonlocal exchange contribution. This does not necessarily mean that our basic approximation $q \ll k_F$ is substantially

TABLE IX. Correlation energies in various approximations (Ry).

	He	Be	Ne	Mg	Ar
Local[a]	−0.29	−0.58	−1.84	−2.19	−3.47
Nonlocal[b]	−0.19	−0.40	−1.36	−1.61	−2.64
Nonlocal[c]	−0.10	−0.20	−0.82	−0.96	−1.60
Exact[d]	−0.08	−0.19	−0.76	−0.86	−1.46

[a] von Barth–Hedin parametrization for E_{xc}.

[b] $f=0.15$ for E_{xc}, $f=0$ for E_x.

[c] $f=0.15$ for E_{xc} and E_x.

[d] See text.

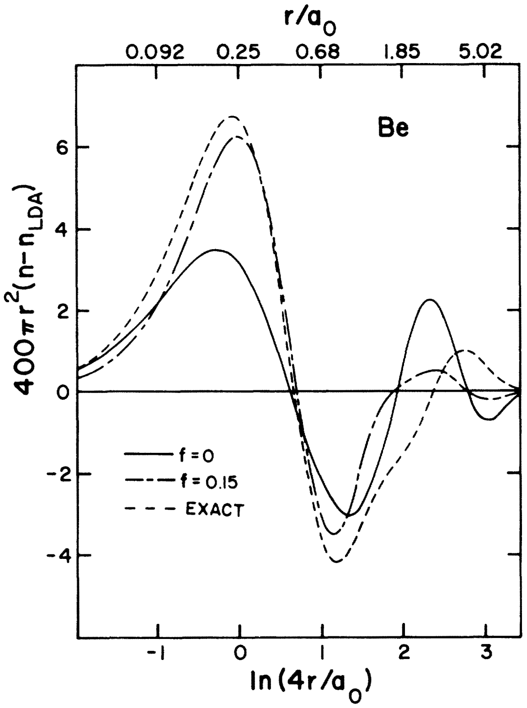

FIG. 7. Be density for "exchange-only." In each case the ordinate is the radial density difference between the indicated calculation and the local-density approximation (×100). The solid curve represents the calculation based on Eq. (4.20) with $f=0$ (thus improperly separating exchange and correlation). The broken curve represents the calculation based on the full Eq. (4.20) ($f=0.15$). The dashed curve is the exact result.

worse for exchange than correlation, but rather that nonlocal exchange is larger in absolute terms than nonlocal correlation even though nonlocal correlation is a ~100% effect. It does mean, however, that the rough method which we used to make the small-k cutoff is not the main source of error.

It is tempting, therefore, to use an *exact* version of exchange and combine this with an approximate version of correlation. Although this idea has undoubtedly occurred to many over the years (see, for example, Ref. 52), the most recent impetus for us to try this has come from Perdew[58] with respect to "exchange-only" and especially from von Barth[59] with respect to Hartree-Fock; the latter has attempted an application of our functional in this connection,[26] but without the benefit of the results of the preceding section.

The approximation which now suggests itself is

$$E^{xc}=E^{x}_{\text{exact}}+(E^{\text{RPA}}_{\text{LDA}})^{c}+a\int d^3r[\vec{\nabla}(\vec{r})]^2(2e^{-F}+18f^2)\,, \tag{5.1}$$

where E^{x}_{exact} is the exact-exchange energy according to (4.3) and $(E^{\text{RPA}}_{\text{LDA}})^c$ is the local-density approximation to the correlation energy in the RPA. The extra term in the curly brackets $(18f^2)$ corrects the correlation energy by the negative energy of extra term in (4.18) as implied by Eqs. (4.11) and (4.12). Similarly,

$$\begin{aligned}v^{xc}(\vec{r})=v^{x}_{\text{exact}}(\vec{r})+(v^{\text{RPA}}_{\text{LDA}})^{c}(\vec{r})+2an^{-1/3}\Bigg[&-18f^2\left[\frac{\vec{\nabla}\cdot\vec{\mathbf{K}}}{n}-\frac{2}{3}\frac{K^2}{n^2}\right]\\&-2e^{-F}\left[\frac{(1-F/2)\vec{\nabla}\cdot\vec{\mathbf{K}}}{n}-\frac{2}{3}-\frac{11F}{6}+\frac{7F^2}{12}\right]\frac{K^2}{n^2}\\&+\frac{F(F-3)\vec{\mathbf{K}}\cdot\vec{\nabla}\,|\vec{\mathbf{K}}|}{2n\,|\vec{\mathbf{K}}|}\Bigg]\,,\end{aligned} \tag{5.2}$$

TABLE X. Correlation energies (Ry) in various approximations using exact exchange in all cases.

	He	Be	Ne	Mg	Ar
Local correlation[a]	−0.30	−0.58	−1.84	−2.19	−3.48
Nonlocal correlation[b] ($f=0.15$)	−0.105	−0.20	−0.82	−0.96	−1.60
Nonlocal correlation[b] ($f=0.17$)	−0.093	−0.18	−0.75	−0.87	−1.45
Exact[c]	−0.084	−0.19	−0.76	−0.86	−1.46

[a] von Barth–Hedin parametrization Ref. 34.
[b] Equation (5.1).
[c] See text.

TABLE XI. Total energies (Ry) of atoms, calculated with exact exchange plus nonlocal correlation.

	He	Be	Ne	Mg	Ar
Calculated ($f=0.15$)	-5.82	-29.34	-257.91	-400.18	-1055.22
Calculated ($f=0.17$)	-5.82	-29.32	-257.84	-400.09	-1055.07
Exact	-5.81	-29.33	-257.84	-400.08	-1055.08

where $v_{\text{exact}}^{x}(\vec{r})$ is the exact-exchange potential and $(v_{\text{LDA}}^{\text{RPA}})^{c}(\vec{r})$ is the RPA correlation potential in the local-density approximation. The other quantities in (5.1) and (5.2) are defined as in (2.31)–(2.35).

We write (5.1) and (5.2) with the same proviso as the similar expressions in the preceding section. That is, the $18f^2$ term must be multiplied in the most general case by an extremely nonlocal functional of the density which is approximately equal to unity for the case of well-localized orbitals, but which is otherwise smaller and approaching zero for fully extended electron-gas-like states. Therefore, we expect (5.1) and (5.2) to give the *correct* nonlocal corrections only for fairly tightly bound systems (or parts of systems). In any case the tests we have made on (5.1) and (5.2) have been restricted to atoms.

In making these tests we have used the exact exchange potentials $v_{\text{exact}}^{x}(r)$ tabulated by Ashamar *et al.*[23] for neutral atoms. Since we are not set up to recalculate v_{exact}^{x} self-consistently once the density distribution is changed by the correlation terms [the remaining terms in the right-hand side of (5.12)], we were forced to use a perturbation procedure. This is in this case, however, a valid procedure because the sum of local *plus* nonlocal correlation *is* very small in atoms (at least once exchange and correlation is properly divided). Our procedure was therefore as follows. For total energies, we calculated the density with $v_{\text{exact}}^{x}(\vec{r})$, and then used that density to evaluate E^{xc} according to (5.1). Similarly, to calculate the density, we first took the density implied by v_{exact}^{x} and evaluated $v^{xc}(\vec{r})$ in (5.2) using this density; this resulting v^{xc} was then used in the Kohn-Sham equations to calculate a new perturbed density. These procedures are guaranteed to give the energy and density correctly to first order in the correlation (local plus nonlocal) parts of (5.1) and (5.2).

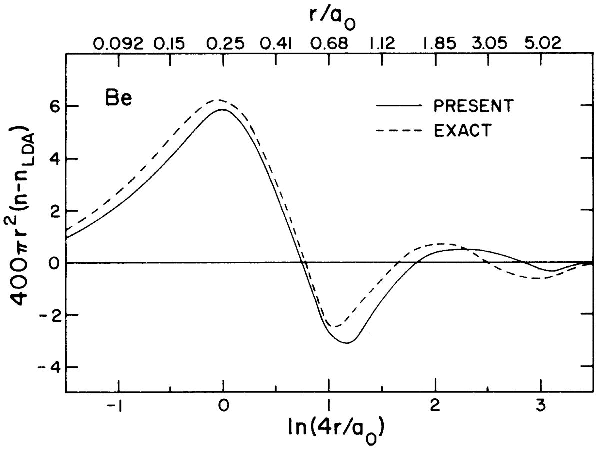

FIG. 8. Density of Be. In each case the ordinate is the radial density difference between the indicated calculations and the local-density approximation (× 100). The solid curve represents the calculation based on Eq. (5.2) ($f=0.15$ and 0.17 virtually indistinguishable on this scale). The dashed line marked "exact" represents the configuration interaction calculations of Ref. 49.

In Table X we show the results for correlation energies of the spinless atoms through argon. These were calculated in the same way as described earlier, except that exact exchange is used, both in the exchange plus approximate correlation calculation, and in the exchange-only calculation which is subtracted from it. The fact that the first two rows of Table X are virtually identical to the first and third rows of Table IX supports our contention that (1) the calculation has been arranged properly so that the functional used for exchange has little effect on the results, and (2) that our perturbation procedure (used in the calculations in Table X but not Table IX) is correct.

In all our previous calculations we have resisted the temptation to adjust f to get a best fit, and except to get a feeling for the sensitivity of calculated values of the choice of f, we have kept to the choice $f=0.15$. However, we have finally reached a point where we believe we have (in the calculations of this section) eliminated all other sources of error which give greater errors than our cutoff procedure. Therefore, now and only now does it make physical sense to make fine adjustments in f. The total correlation energy is fairly sensitive to this choice in percentage terms because of the near cancellation between the nonlocal part which depends on f and the local part which does not. Nevertheless, our original choice of $f=0.15$ was obviously quite good. In Table X we also show the correlation energies calculated for the choice $f=0.17$, which appears to be a slight improvement.

TABLE XII. The eigenvalue (Ry) of the Kohn-Sham equations for atoms, calculated with exact exchange plus nonlocal correlation ($f=0.15$).

	He	Be	Ne	Mg	Ar
1*s*	−1.92	−8.34	−61.67	−92.68	−288.88
2*s*		−0.70	−3.56	−6.34	−22.44
2*p*			−1.83	−3.87	−17.61
3*s*				−0.60	−2.33
3*p*					−1.31

In Table XI we show the total ground-state energies calculated for these elements, using exact exchange plus the correlation of Eq. (5.1) with $f=0.15$ and 0.17. It is apparent that the agreement is very good and therefore provides further evidence for the correctness of the scheme.

Next we have used (5.2) to calculate the density of beryllium and have compared it in Fig. 8 with the exact beryllium density (what is plotted is the deviations from LDA). We note that our approximation not only reproduces all the trends correctly, but also that it is quantitatively a good approximation to the true density in that it, for the most part (except near places where the true error in LDA changes sign), reduces the LDA error of several percent by an order of magnitude or so. We feel that these results for the density as well as the results for the energies provide strong evidence for the correctness of our approximation scheme.

Finally, we give in Table XII our calculated values for the Kohn-Sham eigenvalues. These were calculated with $f=0.15$. Although we now feel on the basis of our correlation-energy results that $f=0.17$ may be a slightly better choice, the difference is not significant enough to recalculate all our results of this and previous sections. There are, of course, no exact results with which to compare our calculated eigenvalues, since the eigenvalues of the Kohn-Sham equations do not give an approximation to the experimental removal energy spectrum either in principle or in practice. We will be very surprised, however, if better calculations in the future do not prove our results in Table XII to be very close to the exact Kohn-Sham eigenvalues.

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