

Exchange and correlation energy in a nonuniform fermion fluid

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Recent results for the surface energy of jelliumlike surfaces are investigated within the functional-density formalism. These results along with first-principles considerations support the contention that the first gradient coefficient of the exchange and correlation energy, in its *unmodified* form, is the proper nonlocal correction to the local-density approximation in extended systems.

The extent to which the local-density approximation^{1,2} (LDA) accounts for the exact exchange and correlation energy in a variety of systems has been, and remains, an area of considerable interest.²⁻¹² Several approaches^{1,7,10-13} have gone beyond the LDA, and claims for their success are well documented. An elegant way of including nonlocality in the exchange and correlation energy is the gradient expansion.^{1,2} Here, by comparing with recent calculations for the surface energy of *extended* systems, we give strong support that the nonlocal form developed initially by us,¹¹ rather than any modified forms,¹³ is the appropriate one to use.¹⁴ We first, however, briefly discuss the main results of our previous investigations which lead us to this conclusion.

The central quantities we considered were the following. The structure factor $S_\lambda(\mathbf{r}, \mathbf{r}')$ given by

$$NS_\lambda(\mathbf{r}, \mathbf{r}') = \langle \phi_\lambda | [\hat{\rho}(\mathbf{r}) - \rho_\lambda(\mathbf{r})][\hat{\rho}(\mathbf{r}') - \rho_\lambda(\mathbf{r}')] | \phi_\lambda \rangle, \quad (1a)$$

its Fourier transform

$$S_\lambda(\mathbf{q}, \mathbf{q}) \equiv \int d^3r \int d^3r' e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')} S_\lambda(\mathbf{r}, \mathbf{r}'), \quad (1b)$$

and the exchange-correlation energy

$$\begin{aligned} E_{xc} &= N \int \frac{d^3q}{(2\pi)^3} E_{xc}(\mathbf{q}) \\ &= \frac{N}{2} \int \frac{d^3q}{(2\pi)^3} v(\mathbf{q}) \int_0^1 d\lambda [S_\lambda(\mathbf{q}, \mathbf{q}) - 1]. \end{aligned} \quad (1c)$$

In Eq. (1) ϕ_λ is the full ground state for the nonuniform interacting fermion system with interparticle interaction $\lambda v(\mathbf{q})$, $\hat{\rho}(\mathbf{r})$ is the density operator, $\rho_\lambda(\mathbf{r})$ is the density given by $\rho_\lambda(\mathbf{r}) = \langle \phi_\lambda | \hat{\rho}(\mathbf{r}) | \phi_\lambda \rangle$, and N the number of fermions. For the interparticle interaction $\lambda v(\mathbf{q})$ we choose $\lambda v(\mathbf{q}) = \lambda 4\pi e^2 / (q^2 + \beta^2)$. A central point of our investigation involved the small q limit of Eqs. (1a) and (1b). By carefully examining a variety of nonuniform systems¹⁵ we were able to show that for a general system with an arbitrary interparticle interaction in the presence of an arbitrary external potential and general level of perturbation in the *thermodynamic* limit,

$$\lim_{q \rightarrow 0} S_\lambda(\mathbf{q}, \mathbf{q}) \neq S_\lambda(q=0, q=0) = \int d^3r \int d^3r' S_\lambda(\mathbf{r}, \mathbf{r}') = 0, \quad (2)$$

(the last equality is simply a statement of conservation of particles [Eq. (1a)]). In other words, the $q \rightarrow 0$ limit of the

structure factor has *nothing* to do with the conservation of the particle sum rule in extended systems. This obviously entirely separates small microscopic size systems (like atoms or molecules) from, as an example, metallic surfaces when we consider the behavior of $S_\lambda(\mathbf{q}, \mathbf{q})$ or $E_{xc}(q)$ at small q . This is so because for microscopic systems the size of the exchange-correlation hole, or equivalently the structure factor $S_\lambda(\mathbf{r}, \mathbf{r}')$, is confined to the size of the atom or molecule under consideration. If the length L_1 reflects the size of the atom, then $|\mathbf{r} - \mathbf{r}'| < L_1$. Therefore, the limit of $S_\lambda(q, q)$ at small q , in the finite nonextended case, must correspond to the conservation of particles, i.e.,

$$\lim_{q \rightarrow 0} S_\lambda(q, q) = S_\lambda(q=0, q=0) = 0. \quad (3)$$

This difference between the finite [Eq. (3)] and infinite [Eq. (2)] systems, discussed above, implies that the small q region in $E_{xc}(q)$ [or $S_\lambda(q, q)$] *must* be *extremely sensitive* to the nonuniform background. In Fig. 1 we illustrate the expecta-

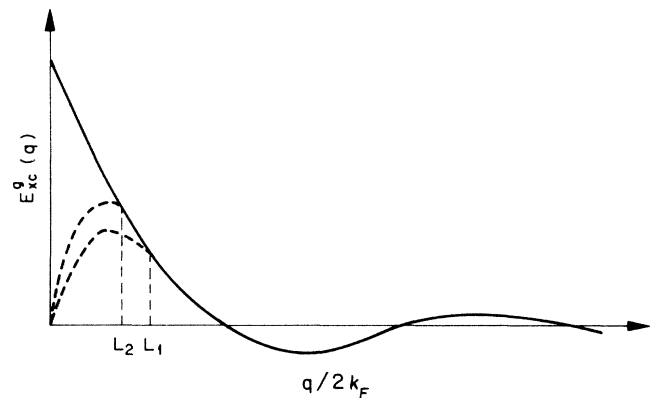


FIG. 1. Sketch of the expected behavior of the wave-vector decomposition for the gradient contribution to the exchange and correlation energy (given by the dashed curves), in two *microscopic* systems of lengths L_1 and L_2 (where $L_2 > L_1$). The solid curve gives the behavior for a *macroscopic* nonuniform electron gas. This small q region has been shown to be very sensitive to the nonuniform perturbation (Ref. 15) and *not* to be determined by any *intrinsic* length scales (like k_F or k_{TF}) of the electron gas (Ref. 15). The graph is therefore to be regarded as only a sketch of this small q region. Clearly, the extended results must overestimate the correlation energy in *microscopic* systems, and the amount overestimated is very sensitive to the system (e.g., L_1 or L_2).

tion in the change of $E_{xc}(q)$ when the size of the system increases from L_1 to L_2 and finally to a macroscopic size given by the solid curve.¹⁵ The solid curve is the wave-vector decomposition (WVD) of the first gradient contribution to $E_{xc}(q)$ [i.e., $E_{xc}^g(q)$]. The interparticle interaction $v(q)$ (in Fig. 1) is taken to be a Coulomb long-range form

$$v(q) = \lim_{\beta \rightarrow 0} 4\pi e^2 / (q^2 + \beta^2) .$$

Figure 1 provides some very important guidelines as we go from nonextended to infinite systems. Clearly, the form derived from electron-gas calculations *must overestimate* the contribution in small systems. In fact, since $E_{xc}^g(q)$ oscillates, as a function of q , we can even imagine changing its overall sign by certain manipulations in the small q region. (An incorrect sign from the electron-gas gradient forms to the exchange-correlation energy of *atomic systems* was recognized a long time ago.¹⁰) To accomplish the necessary changes in atomic systems, the long-wavelength limit of $E_{xc}^g(q)$ was modified,¹³ as illustrated in Fig. 1. However, forcing the long-wavelength limit to vanish at small q can only be justified for finite systems. There is no such justification for semi-infinite or infinite systems due to the subtle role played by the thermodynamic limit [Eq. (1)]. We might still ask whether such modifications can be justified for extended systems by numerical results; we show that such calculations give no support to such contentions.

Before we turn to such numerical considerations it is interesting to relate the above conclusions to previous considerations. It has been generally recognized that localized systems, with their discrete spectrum, are fundamentally different from extended systems, with the corresponding continuous single-particle excitations.^{10,11,16} The latter are much more akin to either the uniform or weakly perturbed uniform interacting electron gas, where such forms are derived. It is, therefore, not surprising that extending such calculations to atoms could, and does, run into considerable difficulties,¹⁰ particularly for the correlation contributions.¹⁰ We would, in fact, expect the correlation energy, derived from the uniform electron gas, to overestimate such contributions in discrete systems (e.g., atoms), since virtual excitations are so much easier for a continuous excitation energy spectrum.¹⁶ It is also not surprising that for exchange alone this problem is less severe, since no virtual excitations (i.e., no energy denominators) exist to sample the discreteness of the eigenvalues. This way of differentiating infinite from finite systems is now further justified using the WVD as illustrated in Fig. 1.

The size of the system is not the only way nonuniformity plays a subtle role in $S_\lambda(q,q)$. In fact, we showed in our previous investigations¹⁵ that any nonuniformity, superimposed on a uniform fermion system, *fundamentally* changes the nature of the structure factor $S_\lambda(r,r')$ in the thermodynamic limit. Such conclusions are true for any interparticle interaction $v(q)$ and general level of perturbation.¹⁷ For $v(q) = 4\pi e^2/q^2$ we traced these differences to the perfect screening sum rule.¹⁸ This sum rule is crucial to the small q limit of $S_\lambda(q,q)$ in the uniform interacting electron gas.¹⁸ Such a sum rule does not exist for the nonuniform counterpart^{15,19} and is the reason that the small- q region is extremely sensitive to the nonuniform environment.¹⁵ These conclusions have been challenged by Langreth and Perdew¹⁵ who consider a nonuniform external potential of a single Fourier component h and take the reverse limits of ours.

An arbitrary nonuniformity, however, contains *all* Fourier components. These points have been dealt with at great length in our previously published articles.¹⁵ As a final point, consider the two-component fermion gas; like an itinerant ferromagnet. Then, even for the uniform case the perfect screening sum rule does not hold for the *individual* components $S_{\uparrow\uparrow}(q,q)$, $S_{\downarrow\downarrow}(q,q)$, and $S_{\uparrow\downarrow}(q,q)$.¹⁹ Therefore, the difference between the extended and finite nonuniform systems is now even more pronounced for each individual structure factor component. The modification of the small q region of the three different gradient contributions to E_{xc} would now be much more arbitrary.

We finally turn to numerical considerations. The problem of correlation is very hard to treat outside the functional-density formalism for nonuniform extended systems in the thermodynamic limit with realistic metallic density profiles. For exchange alone such solutions for surface jellium profiles (or more precisely accurate model representations) do exist, and they have been studied in great detail.^{17,20-22} It is clear that the nonlocal corrections reasonably account for the full exchange energies. Recently, moreover, two calculations for the correlated surface energy of a jelliumlike density profile have appeared.^{23,24} The results are expected to provide a valuable indication of the magnitude for the nonlocal contribution to the total exchange and correlation energy. In Table I these results are presented along with the gradient expansion (GE) as first proposed by us, column 7, and the recent modified gradient forms, MGE, column 6. Obviously, the two calculations^{23,24} *both* point to a *much* larger contribution for the nonlocal exchange and correlation surface energy than previously suggested (column 6) and provide no *numerical* justification either for the modification at small q in extended systems. On the other hand, the gradient expansion, as first proposed (column 7), significantly improves the local-density values of Lang and

TABLE I. Comparison of the surface energies obtained for the jellium model by Lang and Kohn (LK, Ref. 32), column 3; Sun, Li, Farjam, and Woo (Ref. 23), column 4; Krotscheck, Kohn, and Qian (Ref. 24), column 5. MGE are the results of Langreth and Mehl (Ref. 13), column 6; and GE are the results of our original gradient form (Ref. 11), column 7. Note that our results contain contributions to all orders and therefore go beyond the RPA. This was also shown in great detail by Hu and Langreth in Ref. 33. All surface energies are given in ergs/cm². In the case of the MGE we took the values for the recommended $f=0.15$. There are two other listed choices for $f=0.12$ and 0.17 and the averaged gradient approximation; all of these give *much* smaller contributions to the nonlocal corrections from ($\frac{1}{2}$ to $\frac{1}{3}$ of ours), and in very poor agreement with, columns 4 and 5. Note also that the results of LK correspond to the Wigner exchange and correlation form for the local-density approximation. Other more recent forms would tend to increase the LK results at $r_s=2.07$ by approximately 100 ergs/cm².

r_s	Metal	LK	SFW	FHNC 0	MGE	GE
2.07	Al	-730	102	-222	-645	-280
2.30	Pb	-130	278	181		170
2.66	Mg	110	309	383		305
3.28	Li	210	363	360		305
3.99	Na	160	204	261	179	210
4.96	K	100	94	159		125
5.23	Rb	85	76	105		105

Kohn. Such improvements are obviously important and we therefore list a convenient parametrized form for these non-local contributions, i.e.,

$$E_{xc} = E_{xc}^{\text{LDA}} + E_{xc}^g, \quad (4a)$$

where the nonlocal gradient contribution is

$$E_{xc}^g = \int d^3r B_{xc}(\rho(\mathbf{r})) |\nabla\rho(\mathbf{r})|^2, \quad (4b)$$

and B_{xc} is written in terms of the unitless quantity¹¹ $C_{xc}(r_s)$, as

$$B_{xc} = \frac{e^2}{\rho(\mathbf{r})^{4/3}} C_{xc}(r_s). \quad (4c)$$

This coefficient $C_{xc}(r_s)$ is listed as a function r_s [$r_s \equiv (3/4\pi\rho)^{1/3}$ in a.u.] in Ref. 11. Here, for convenience of application, we list the interpolation form

$$C_{xc}(r_s) = 10^{-3} \frac{2.568 + ar_s + br_s^2}{1 + cr_s + dr_s^2 + 10br_s^3}, \quad (4d)$$

with $a = 23.266$, $b = 7.389 \times 10^{-3}$, $c = 8.723$, and $d = 0.472$. This form accounts accurately for the required values of $C_{xc}(r_s)$.²⁵

We expect, of course, the same conclusions to carry in multicomponent systems. As discussed above, there is again no reason for any modifications at small q . The non-local contributions now become

$$E_{xc} = \int d^3r [B_{xc}^{\uparrow\uparrow}(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})) |\nabla\rho_{\uparrow}(\mathbf{r})|^2 + B_{xc}^{\uparrow\downarrow}(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})) |\nabla\rho_{\downarrow}(\mathbf{r})|^2 + B_{xc}^{\downarrow\downarrow}(\rho_{\uparrow}(\mathbf{r}), \rho_{\downarrow}(\mathbf{r})) \nabla\rho_{\uparrow}(\mathbf{r}) \cdot \nabla\rho_{\downarrow}(\mathbf{r})]. \quad (5)$$

For an itinerant ferromagnet, results in the high-density limit (HDL) were derived first in Ref. 26. A convenient interpolation form was listed in Ref. 27. From the single component results of $C_{xc}(r_s)$, we might expect the HDL results for the two spin components to still be relevant at metallic densities, but the extension to bulk densities¹¹ is warranted. For the multicomponent electron-hole droplet, where the effective densities are high, we expect our results to be very important. The appropriate forms for silicon and germanium are presented in Refs. 28 and 29.

Metallic surfaces, itinerant ferromagnets, and the electron-hole droplet are just a few examples of nonuniform systems where the original nonlocal forms are appropriate and important.³⁰ We conclude with a few remarks about the crossover from finite to infinite systems as $L_1 \rightarrow L_2 \rightarrow \infty$ in Fig. 1.

What first-principles considerations,¹⁵ and now the recent numerical calculations,^{23,24} have conclusively shown is that the previous potential,¹³ which was applied to closed-shell atoms, cannot be applied to extended systems. It is obviously not a valid universal functional of the density, but is limited to a narrow class of atomic systems. The difficulty of guessing a correct functional is enormous. There are endless possible forms to consider, and the chance of pulling out the right one is very small indeed. Only first-principles calculations can lead to some progress, and the nonlocal form we suggest does do that. The WVD can still play an important role in studying the crossover from extended to finite-size systems. We are presently trying to see how the nonlocal contributions get corrected for the finite-size effects. In other words, what are the corrections to $B_{xc}(\rho, L)$ as a function of the size L of the system? Here the WVD helps differentiate between $q < 1/L$ and $q > 1/L$; in the large q region the finite-size corrections are expected to play a minor role. Finally, it still remains to resolve the most intriguing question concerning the convergence of these expansions. Specifically, it is well known that the polarization functions¹⁵ $\Pi(\mathbf{h})$ rapidly deviate from their small power expansions in \mathbf{h} . This is even true for the kinetic energy alone where the convergence has been closely scrutinized. Apparently the continuation $\rho \rightarrow \rho(\mathbf{r})$ plays a crucial role in the convergence of both the LDA and higher gradient corrections.³¹

In conclusion, the recent numerical calculations of the surface energy of metals lends support for the gradient expansion in the form originally suggested.¹¹ These forms make a significant improvement to the LDA and should be included in many of the extended systems discussed here.

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¹³D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. **47**, 446 (1981); Phys. Rev. B **28**, 1809 (1983). (The improvement achieved in several closed-shell atomic systems is predicated on using the RPA local-density exchange-correlation energy and is based on claimed cancellations between the LDA and nonlocal corrections. This, however, cannot be generally true, since the LDA and nonlocal contributions involve totally different considerations; the LDA is independent of an imposed external potential in an otherwise uniform system, while the gradient corrections owe their entire existence to such a potential. We, therefore, do not believe that all past RPA advances in the LDA should be ignored in favor of such an arbitrary prescription. We believe that one should do the best on both the LDA and the nonlocal corrections. This is also in agreement with recent results of Ref. 24 that finds non-RPA contributions very important to the surface energy of simple metals.)

¹⁴Direct comparison with experimental measurement in extended

- systems cannot as yet conclusively resolve such delicate questions. See, for example, J. Ferrante and J. R. Smith, Phys. Rev. B **19**, 3911 (1979), where the unmodified gradient (Ref. 11) form significantly improves the surface energy of metals, or R. Car and U. von Barth, in *Many-Body Phenomena at Surfaces*, edited by D. Langreth and H. Suhl (Academic, New York, 1984), p. 31, which indicates that the modified forms (Ref. 13) give improvement for the cohesive energy in bulk Si. (Note that Si as a nonuniform system is different, since the electron-hole spectrum of excitations has a gap.)
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- ²⁵We note that the modified gradient form (Ref. 13) has a drastically different density dependence from this $C_{xc}(r_s)$ when applied to a metal surface. While the $C_{xc}(r_s)$ in Eq. (4d) has a weak dependence on r_s (Ref. 11) the modified effective form for $C_{xc}(r_s)$ drops by ≈ 5 from the high-density value (at $r_s = 0$) to $r_s = 2$.
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