Surface energy of a bounded electron gas: Analysis of the accuracy of the local-density approximation via *ab initio* self-consistent-field calculations

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We report an *ab initio* evaluation of the surface energy of a simple metal, performed via a coupling-constant integration over the dynamical density-response function. The rapid rate of change of the electron density at the surface is treated exactly. Long-range correlations are treated self-consistently in the random-phase approximation; short-range correlations are included in time-dependent local-density-functional theory. Our results provide a numerical measure of the error introduced by the usual local-density approximation; this error is found to be small. [S0163-1829(98)02411-4]

Since the pioneering work of Lang and Kohn,[1] the calculation of the surface energy of a metal has been the subject of long-standing interest. These authors were the first to include the crucial effects of exchange and correlation self-consistently within the local-density approximation (LDA) of density-functional theory (DFT).[2] Lang and Kohn also discussed the effect of the crystal lattice, whose full inclusion within the LDA poses no difficulties of principle these days. By contrast, the question of the impact of nonlocal Coulomb correlations, and their interplay with the strong charge inhomogeneity at the surface, has remained unsettled over the years.[3–9]

Recent calculations have rekindled the controversy on the question of the quality of the LDA surface energy. A many-body scheme that starts from a physically motivated model of the correlated ground state, and treats the interactions via a Fermi hypernetted-chain approximation (FHNCA),[10] has yielded surface energies that are significantly higher than the LDA results of Lang and Kohn.[1] By contrast, the surface energies obtained in density-functional calculations[11] based on the use of the Langreth-Mehl nonlocal functional[12] are much closer to the LDA result. Finally, although very recent quantum Monte Carlo (QMC) calculations[13] agree with the latter nonlocal density functional results[12] for high densities ($r_s \leqslant 2.07$), they agree with the FHNCA for lower densities ($r_s \geqslant 3.25$).

The purpose of this paper is to establish, in a controlled way, the impact of nonlocality on the surface energy of an electron gas. To this end we carry out nonlocal and local calculations within exactly the same conditions, i.e., we consider the LDA as a special case of the general nonlocal formalism based on a coupling-constant integration over the dynamical density-response function. First, the effects of nonlocal correlations are investigated fully self-consistently within a well-defined many-body framework, the random-phase approximation (RPA).[14] Our side-by-side calculation, in which the same diagram is used to generate the local and nonlocal surface energies, shows that the LDA is quite accurate over the entire density domain appropriate to metals ($r_s = 2-6$). Of course, the absolute values of our RPA energies cannot be expected to be more reliable than, say, the QMC surface energies. However, the significance of our results lies in the elucidation of the *difference* between nonlocal and local surface energies. We also explore the impact of short-range correlations by invoking a time-dependent extension of local density-functional theory (TDLDA).[15] The TDLDA vertex introduces an element of arbitrariness, since it contains no dynamical effects. Thus, again, we are less interested in the absolute value of the TDLDA surface energy than we are in its *difference* with its local counterpart; again, we evaluate this difference in an unambiguous way. Our TDLDA results support the conclusion drawn from our RPA results that the error introduced by the LDA is not large.

The ground-state energy of an interacting electron system can be written as a functional of the electron number density $n(\mathbf{r})$,[2]

$$E[n] = E_k[n] + E_{\rm es}[n] + E_{\rm xc}[n], \tag{1}$$

where $E_k[n]$ is the kinetic energy of a noninteracting system with the same density and $E_{\rm es}[n]$ is the Hartree electrostatic energy. The exchange-correlation (xc) energy, $E_{\rm xc}[n]$, can be obtained from a coupling constant-integration over the interaction energy. We follow Langreth and Perdew[7] and choose the coupling constant such that the density is maintained at its fully interacting value while the electron-electron interaction strength is varied from $\lambda = 0$ to $\lambda = 1$. The fluctuation-dissipation theorem then leads us to the result that

$$E_{\rm xc}[n] = \frac{e^2}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|} \times \left[-\frac{\hbar}{\pi}\int_0^\infty d\omega \chi_\lambda(\mathbf{r},\mathbf{r}';i\omega) - n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \right], \tag{2}$$

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where $\chi_\lambda(\mathbf{r},\mathbf{r}';\omega)$ is the density-response function.

If the Coulomb correlations are ignored altogether, Eq. (2) reduces to the expression

$$E_x[n]=\frac{e^2}{2}\int d^3r\int d^3r'\,\frac{1}{|\mathbf{r}-\mathbf{r}'|}\times\left[-\frac{\hbar}{\pi}\int_0^\infty d\omega\chi^0(\mathbf{r},\mathbf{r}';\mathrm{i}\omega)-n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\right], \tag{3}$$

where

$$\chi^0(\mathbf{r},\mathbf{r}';\omega)=2\sum_{i,j}\frac{\theta(E_F-E_i)-\theta(E_F-E_j)}{E_i-E_j-\hbar(\omega+\mathrm{i}\eta)}\times\psi_i(\mathbf{r})\psi_j^*(\mathbf{r})\psi_j(\mathbf{r}')\psi_i^*(\mathbf{r}') \tag{4}$$

is the density-response function for noninteracting electrons. For *inhomogeneous* systems Eq. (3) coincides with the Fock exchange energy only if the wave functions $\psi_i(\mathbf{r})$ are the solutions of the nonlocal Hartree-Fock equation.

Actually, Eq. (4) can be interpreted in a more general context as giving the density-response to an appropriate mean-field set up by the dynamical polarization of the Fermi sea. In the particular case of the RPA, the single-particle wave functions $\psi_i(\mathbf{r})$ entering Eq. (4) are strictly the self-consistent eigenfunctions of the one-electron Hartree Hamiltonian. In time-dependent density-functional theory,[16] the ''noninteracting'' electrons in question are described by the solutions of the time-dependent counterpart of the Kohn-Sham equation;[2] in usual practice, these amplitudes are approximated by standard LDA wave functions.[17] Both approaches to the evaluation of the polarizability $\chi^0(\mathbf{r},\mathbf{r}';\omega)$ will be considered in our numerical study of the surface energy of a simple metal.

In both RPA and TDLDA the response function satisfies the integral equation[18]

$$\chi_\lambda(\mathbf{r},\mathbf{r}';\omega)=\chi^0(\mathbf{r},\mathbf{r}';\omega)+\int d\mathbf{r}_1\times\int d\mathbf{r}_2\chi^0(\mathbf{r},\mathbf{r}_1;\omega)\lambda V(\mathbf{r}_1,\mathbf{r}_2)\chi_\lambda(\mathbf{r}_2,\mathbf{r}';\omega). \tag{5}$$

In the RPA, the effective electron-electron interaction $V(\mathbf{r}_1,\mathbf{r}_2)$ is just the bare Coulomb potential. In TDLDA,

$$V(\mathbf{r}_1,\mathbf{r}_2)=\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}+\frac{dV_{\mathrm{xc}}(\mathbf{r}_1)}{dn(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2), \tag{6}$$

V_{xc} being the local xc potential. The combination of Eqs. (2) and (5) defines either the TDLDA or the RPA exchange-correlation energy, depending on whether or not the Coulomb interaction is ''dressed'' according to Eq. (6). This dressing corresponds to the inclusion of short-range correlations, which are ignored in RPA.

We consider a jellium slab of thickness a and density $\overline{n}_+=q_F^3/3\pi^2$, where $q_F=(9\pi/4)^{1/3}/(r_s a_0)$ is the Fermi wave vector, r_s is the Wigner-Seitz radius, and a_0 is the Bohr radius. The slab is translationally invariant in the plane of the surface, which is assumed to be normal to the z axis. Thus the single-particle wave functions are of the form

$$\psi_i(\mathbf{r})=\frac{1}{\sqrt{A}}\phi_i(z)e^{\mathrm{i}\mathbf{q}_\parallel\cdot\mathbf{r}_\parallel}, \tag{7}$$

where $\mathbf{q}_\parallel$ is a wave vector parallel to the surface and A is the normalization area. The wave functions $\phi_i(z)$ describe motion normal to the surface, and are obtained self-consistently with the effective one-electron potential, $V_{\mathrm{eff}}(z)$. In the RPA, V_{eff} consists of just the Hartree potential $V_{\mathrm{es}}(z)$; in TDLDA,

$$V_{\mathrm{eff}}(z)=V_{\mathrm{es}}(z)+V_{\mathrm{xc}}(z). \tag{8}$$

For reference, we recall that in the simplest non-self-consistent microscopic model of the surface, the infinite-barrier model (IBM), $V_{\mathrm{eff}}(z)$ is replaced by an infinite square barrier, and the functions $\phi_i(z)$ are simply sines.

A solution of Eq. (5) for a self-consistent description of the surface potential was given some time ago.[19] We assume that $n(z)$ vanishes at a distance z_0 from either jellium edge, and expand the wave functions $\phi_i(z)$ in a Fourier sine series; z_0 is chosen sufficiently large for the physical results to be insensitive to the precise value employed. We introduce a double-cosine Fourier representation for the density-response function, and also for the Coulomb potential and the Dirac δ function entering Eq. (2).[20] The use of this representation allows us to perform analytically the integrals in Eq. (2) involving the coordinate normal to the surface; the integrals over parallel-momentum transfers, over energy transfers, and over the coupling constant are performed numerically. The total energy given by Eq. (1) is evaluated in a similar way. Subtracting from the total energy the corresponding result for a homogeneous electron gas of density $\overline{n}_+$, $E^H[\overline{n}_+]$, we obtain the surface energy

$$\sigma=\frac{1}{2A}\{E[n(z)]-E^H[\overline{n}_+]\}. \tag{9}$$

The LDA is obtained from the above nonlocal formalism by replacing the response function entering Eq. (2) by its counterpart for a homogeneous electron gas with the local value of the density. This replacement leads us to the result that[20]

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n]=\frac{1}{a}\int_0^{a+2z_0}dz E_{\mathrm{xc}}^H[n(z)]. \tag{10}$$

Equation (10), with $E_{\mathrm{xc}}^H[n(z)]$ evaluated on the basis of (homogeneous electron gas-) RPA and TDLDA density-response functions, calculated for the local value of the density $n(z)$ obtained self-consistently with Hartree and LDA effective potentials, yields our RPA- and TDLDA-based LDA surface energies. We will consider these local results together with the LDA results of Lang and Kohn[1] — which we also obtain from Eq. (10) through the use of the Wigner interpolation formula for $E_{\mathrm{xc}}^H[n(z)]$.[21]

Great care was exercised to ensure that our slab calculations are a faithful representation of the surface energy of a semi-infinite medium. This issue is important, in view of the subtle cancellations that exist among the various contributions to the surface energy; furthermore, these contributions

TABLE I. Exchange-correlation (σ_{xc}) and total (σ) nonlocal surface energies obtained in RPA and TDLDA, and their local counterparts. Units are erg/cm^2.

	RPA				TDLDA			
r_s	σ_{xc}	σ_{xc}^{LDA}	σ	σ^{LDA}	σ_{xc}	σ_{xc}^{LDA}	σ	σ^{LDA}
2.0	4657	4583	-126	-200	3533	3353	-686	-866
2.07	4154	4080	73	-1	3125	2959	-446	-612
3.0	1203	1175	477	449	840	763	301	224
4.0	467	454	281	268	295	261	198	164
5.0	226	219	164	157	130	111	117	98
6.0	125	121	100	96	65	54	71	60

are oscillatory functions of the slab width a. (The amplitude of the oscillations decays approximately linearly with a; their period equals $\lambda_F/2$, $\lambda_F = 2\pi/q_F$ being the Fermi wavelength.)

For each value of r_s we have actually considered three different values of a. One such value, a_n, is the threshold width for which the nth subband for the z motion is first occupied; for this width the surface energy is a local minimum. The other two values of the slab width, $a_n^- = a_n - \lambda_F/4$ and $a_n^+ = a_n + \lambda_F/4$, correspond to the two local maxima about the minimum. Utilizing the relation[20]

$$\sigma = \frac{\sigma_n^- + \sigma_n + \sigma_n^+}{3}, \tag{11}$$

we are able to extrapolate our calculated surface energy to the infinite-width limit. This procedure was first tested, with values of n up to 200, for the IBM, for which analytical insight is possible by virtue of the simple nature of the one-electron wave functions.[20] The results presented below correspond to slabs with $n=12$, for which $a \approx 5 - 6\lambda_F$, depending on r_s. Based on this procedure, we estimate that the numerical error introduced by our slab simulations corresponds to one unit in the last digit of all the entries in Table I. [We remark that our results were found to be insensitive to the precise value of the number of sines s_{max} kept in the expansion of the wave functions $\phi_i(z)$, for $s_{max} \geqslant 280$.]

The key results of our work can be readily grasped from Fig. 1, in which we show the surface energy as a function of r_s. Consider first the RPA. The reasons for the significance of our RPA calculations are: (i) the effects of long-range correlations are included fully self-consistently with the electron density profile (which, we recall, is evaluated in the Hartree approximation); (ii) the nonlocal and local calculations are carried out within one and the same density-response framework; (iii) this framework is devoid of any ambiguities in the treatment of the many-body problem. *It is clear from Fig. 1 that the local RPA surface energy differs little from its nonlocal counterpart over the entire metallic range of densities.*

Next, we consider the effects of the short-range correlations built into the xc potential V_{xc}. In the full TDLDA treatment, this effect is included in both the one-electron potential of Eq. (8) and the electron-electron interaction of Eq. (6). (We evaluate V_{xc} with use of the Perdew and Zunger parametrization[22].) Overall, the main impact of the inclusion of xc is via Eq. (8), which, through self-consistency, yields a more abrupt electron density profile at the surface, relative to the Hartree profile. This leads to the large lowering of the surface energy, relative to the RPA, which we observe in Fig. 1. For completeness, in Fig. 1 we show both the full TDLDA (solid line), and the result obtained upon including xc in Eq. (8) but not in Eq. (6) (dashed line); clearly, the impact of the xc vertex is smaller than the effect of the inclusion of xc in the electron density profile.

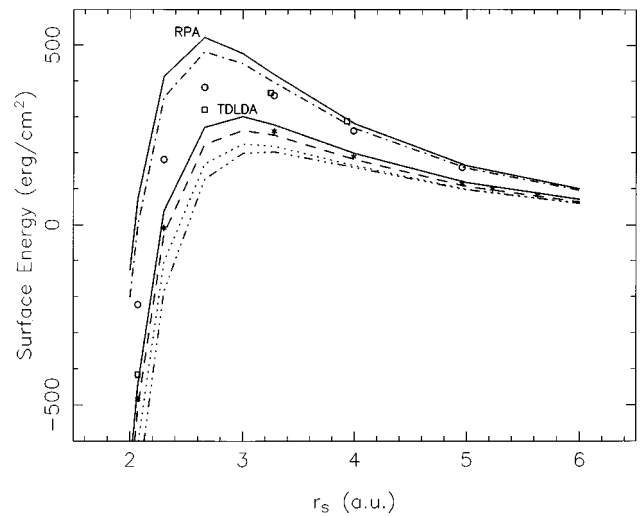

FIG. 1. Nonlocal RPA and TDLDA surface energies (solid lines), as functions of r_s. The dashed line is the TDLDA result obtained upon excluding the xc vertex from Eq. (6). Dashed-dotted and dotted lines represent the local RPA and TDLDA surface energies, respectively. The dashed-dotted-dotted-dotted line represents the Lang-Kohn surface energy of Ref. 1. Open circles, stars and open squares are results taken from Refs. 10, 12, and 13, respectively.

As was the case above with the RPA calculations, *the difference between nonlocal* (solid line) *and local* (dotted line) *TDLDA surface energies is relatively small*. More specifically, the error introduced by the LDA is of the order of 50% smaller than the error one would impute to the local approximation on the basis of the nonlocal FHNCA results[10] (open circles in Fig. 1), particularly in the crucial high-density region ($r_s \approx 2$).

It is apparent from Fig. 1 that our nonlocal TDLDA surface energies agree well, *for all densities*, with those obtained by Zhang, Langreth, and Perdew[12] using the nonlocal Langreth-Mehl[11] xc functional. By contrast, while the surface energy obtained via QMC techniques[13] is close to either set of results for $r_s = 2.07$, for lower densities the QMC surface energies are appreciably larger; in fact, they are close to the FHNCA values.

It is interesting to note that our TDLDA-based LDA surface energies agree closely with the LDA calculations of Acioli and Ceperley.[13] (Our results can also be reproduced from Eq. (10) with use of the Perdew and Zunger parametrization of $E_{xc}^H[n(z)]$.[22]) Thus, while from the QMC results of Ref. 13 one would conclude that the error introduced by the LDA is, for $r_s > 3.25$, rather significant, this is not what transpires from our results—most particularly, from our RPA calculations.

We note that the difference between our TDLDA-based LDA results and the local Lang-Kohn surface energies

(dashed-dotted-dotted-dotted line) is simply a consequence of the use by these authors[23] of the Wigner formula for correlation.[21] The much larger difference between Lang-Kohn surface energies and our RPA-based LDA results reflects, again, the impact of xc on the electron density profile at the surface.

If the surface energy is obtained from Eq. (3) [not Eq. (2)], in conjunction with an *exchange-only* correction to the Hartree barrier in Eq. (8), we obtain nonlocal surface energies that are close to the Hartree-Fock results reported by Krotscheck and co-workers.[10] By contrast, the nonlocal *correlation* contribution to the surface energy reported in Ref. 10 is significantly higher than our *ab initio correlation* surface energy; as a result, the FHNCA surface energies are much higher than our nonlocal TDLDA values, as shown in Fig. 1. The FHNCA and RPA surface energies turn out to be quite close, at low densities, because of compensation between the effect of xc in the effective one-electron potential, which is absent in the RPA, and the very large FHNCA nonlocal correlation surface energy.

In conclusion, we have presented *ab initio* calculations of the surface energy of a bounded electron gas. The unambiguous nature of the comparison of local versus nonlocal surface energies made possible by our self-consistent RPA calculations leads us to the conclusion that the LDA does, within the RPA, work. We have also evaluated the *difference* between nonlocal and local TDLDA surface energies, and the results so obtained support the conclusion that the error introduced by the LDA is, within the TDLDA, not large, over the whole range of electron densities appropriate to metals. Further progress in the quantitative *ab initio* evaluation of this *difference* requires improvements in the treatment of dynamical many-body correlations beyond the scope of Eq. (6).

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[1] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).
[2] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. Sham, **140**, A1133 (1965).
[3] J. Harris and R. O. Jones, Phys. Lett. A **46**, 407 (1974); J. Phys. F **4**, 1170 (1974).
[4] G. D. Mahan, Phys. Rev. B **12**, 5585 (1975).
[5] E. Wikborg and J. E. Inglesfield, Solid State Commun. **16**, 335 (1975); Phys. Scr. **15**, 37 (1977).
[6] N. D. Lang and L. J. Sham, Solid State Commun. **17**, 581 (1975).
[7] D. C. Langreth and J. P. Perdew, Solid State Commun. **17**, 1425 (1975); Phys. Rev. B **15**, 2884 (1977).
[8] M. Rasolt and D. J. W. Geldart, Phys. Rev. Lett. **35**, 1234 (1975); J. H. Rose, Jr., H. B. Shore, D. J. W. Geldart, and M. Rasolt, Solid State Commun. **19**, 619 (1976).
[9] J. P. Perdew, D. C. Langreth, and V. Sahni, Phys. Rev. Lett. **38**, 1030 (1977).
[10] E. Krotscheck, W. Kohn, and G.-X. Qian, Phys. Rev. B **32**, 5693 (1985); E. Krotscheck and W. Kohn, Phys. Rev. Lett. **57**, 862 (1986).
[11] Z. Y. Zhang, D. C. Langreth, and J. Perdew, Phys. Rev. B **41**, 5674 (1990).
[12] D. C. Langreth and M. J. Mehl, Phys. Rev. Lett. **47**, 446 (1981).
[13] X.-P. Li, R. J. Needs, R. M. Martin, and D. M. Ceperley, Phys. Rev. B **45**, 6124 (1992); P. H. Acioli and D. M. Ceperley, *ibid.* **54**, 17 199 (1996).
[14] See, e.g., D. Pines, *Elementary Excitations in Solids* (Addison Wesley, New York, 1963), Chap. 3.
[15] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).
[16] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984); E. K. U. Gross and W. Kohn, Adv. Quantum Chem. **21**, 255 (1990).
[17] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).
[18] As a consequence of having chosen the coupling constant such that the electron density is maintained at its fully interacting value, $V_\lambda(\mathbf{r}_1,\mathbf{r}_2)$ can be replaced by $\lambda V(\mathbf{r}_1,\mathbf{r}_2)$.
[19] A. G. Eguiluz, Phys. Rev. Lett. **51**, 1907 (1983); Phys. Scr. **36**, 651 (1987).
[20] J. M. Pitarke and A. G. Eguiluz (unpublished).
[21] E. P. Wigner, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).
[22] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[23] Differences between our TDLDA-based LDA results and the Lang-Kohn surface energies also appear as a result of these authors evaluating the xc potential of Eq. (8) by using the Wigner parametrization. However, we have found that the various contributions to both local and nonlocal exchange-correlation surface energies are rather insensitive to the choice of the correlation potential of Eq. (8), and that total surface energies are even more insensitive to this choice.