Corrections to the Local Density Approximation: Gradient Expansion versus Wave-Vector Analysis for the Metallic Surface Problem

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We present strong evidence that the first gradient correction to the local density approximation for exchange and correlation is inappropriate near physical metallic surfaces, in that it fails to improve the energy and worsens the density profile. Further evidence is presented for the validity of the wave-vector analysis procedure, in that it is shown to be correct both for slowly varying and for rapidly varying density profiles.

The approximation that the exchange-correlation energy is a local functional of the electronic density [local density approximation (LDA)][1] is by now widely used in the calculation of ground-state properties of nonuniform systems, and particularly of solid surfaces.[2] The LDA is valid *a priori* only when the density varies slowly on the scales of the local Fermi wavelength and screening length. The justifications for the use of this approximation have therefore been *a posteriori*, in the form of comparisons between LDA results and exact results for solvable models.

Although the gradient expansion[1] provides a systematic *a priori* method for calculating corrections to the LDA, even the lowest-order coefficient in it had not been known except in the high-density limit. It is no surprise then that, since the recent calculation of this coefficient at metallic densities,[3] a widespread use of the gradient expansion in the calculation of surface properties has occurred.[4-8] We might expect the use of this gradient correction to increase greatly, especially since it is rather easy to incorporate into existing LDA calculational schemes. In this Letter, therefore, we present strong evidence that such increased use of the gradient correction would be inappropriate. Even at surface density profiles as slowly varying as $r_s = 2$ jellium, we suggest that the gradient correction gives no improvement to the energy and actually worsens the density profile.

Our procedure is as follows: (1) Find a system whose density can be made to vary in space as rapidly or slowly as we may wish, with physical metallic surfaces corresponding to the intermediate case; (2) calculate the surface exchange-correlation energy in the random phase approximation (RPA) for this system; (3) calculate the difference between (2) and the corresponding RPA calculation in LDA; and (4) compare the results of (3) with the RPA first gradient correction to the exchange-correlation energy of the same system. We do this for continuously increasing density gradients, and find that the results of (4) depart from those of (3) before density variations as rapid as those of a typical surface are reached.

The only problem with this procedure is that step (2) is prohibitively lengthy and must be done approximately. For this we use the wave-vector analysis method developed earlier by two of us.[9,10] This involves an exact and rigorous decomposition of the surface exchange-correlation energy σ_{xc} into contributions $\sigma_{xc}(K)$ from density fluctuations of different wave vector K. At both large and small K, $\sigma_{xc}(K)$ could be found exactly, leaving as the only approximation an interpolation between the two limits. The simple interpolation scheme used in Ref. 9 and made analytic in Ref. 10 proved to be accurate to about 1% when tested against the exactly solvable infinite-square-barrier model,[11] which represents the limit of rapid density variation. A further test of the wave-vector interpolation is provided in the present work, where it is found to agree with the gradient expansion for slowly varying densitites, for which the gradient expansion is valid *a priori*. We thus think it extremely unlikely that the wave-vector method could go awry in the intermediate ∇n

range of physical interest, and treat it as sufficiently accurate to use in step (2) above.

We restrict our testing ground, although presumably not the implication of our tests, to systems whose density profile $n(x,y,z)=n(x)$ is a function of x only, which changes from a bulk value $n_0=(4\pi r_s^3 a_0^3/3)^{-1}$ at $x=-\infty$ to zero at $x=+\infty$. We use the linear potential model[12,13] to produce single-particle Lang-Kohn[2] wave functions $\psi_i(\vec{x})$ which in turn generate $n(x)$. Thus our ψ_i's are the eigenfunctions of $-(\hbar^2/2m)\nabla^2+v(x)$, where

$$v(x)/\epsilon_F = k_F x/y_F \tag{1}$$

for $x>0$ and $v(x)=0$ otherwise, with $\epsilon_F=\hbar^2 k_F^2/2m$ and k_F the Fermi energy and wave vector, respectively. Here y_F is a dimensionless parameter at our disposal, allowing us to go continuously from a rapidly varying density profile to a slowly varying one. This is illustrated in Fig. 1. The value $y_F=0$ corresponds to the infinite-square-barrier model, with $|\nabla n|/2k_F(n)n\approx 1$ at the jellium edge (where most of the gradient contribution arises), while $y_F\approx 8$ corresponds to $|\nabla n|/2k_F(n)n\approx 0.1$; the latter is small enough that the accuracy of the gradient correction cannot be doubted.

The potential (1) could be regarded in two ways: (a) as the fully self-consistent external + Coulomb + exchange-correlation potential corresponding to an (unknown) external potential which gives rise to the profiles of Fig. 1; or (b) merely as a simple way to generate wave functions ψ_i with which to evaluate the surface energy functional, which in turn is minimized with respect to variations of y_F.

In the spirit of view (a) above we generate energy curves of surface exchange-correlation energy versus y_F for the various approximations. For the LDA we use the standard expression

$$\sigma_{xc}^{\mathrm{LDA}} = \int_{-\infty}^{\infty} dx\,[n(x)\epsilon_{xc}(n(x)) - n_0\epsilon_{xc}(n_0)\theta(x_0-x)], \tag{2}$$

where $\epsilon_{xc}(n)$ is the RPA exchange-correlation energy per electron of a uniform electron gas of density n. The jellium edge x_0 is determined from the condition $\int_{-\infty}^{\infty} dx\,[n(x)-n_0\theta(x_0-x)]=0$. We need also the wave-vector analysis form

$$\sigma_{xc} = \int_0^{\infty} d(K/2k_F)\gamma(K) \tag{3}$$

with $\gamma(K)$ determined as in Refs. 9 and 10, and the gradient expansion

$$\sigma_{xc} = \sigma_{xc}^{\mathrm{LDA}} + \int_{-\infty}^{\infty} dx\,B_{xc}(n(x))|\nabla n|^2 \tag{4}$$

with B_{xc} taken from Ref. 3.[14] The results of the comparison are shown in Fig. 2.

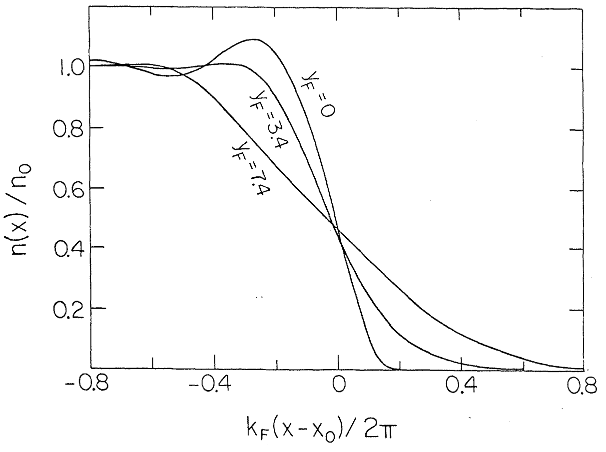

FIG. 1. Electron density profiles of the linear potential model.

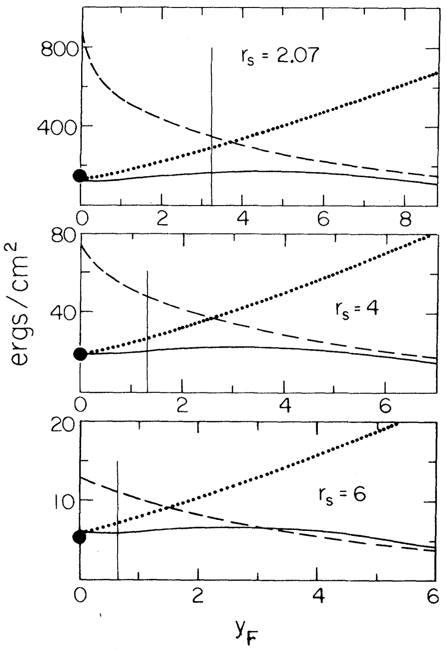

FIG. 2. The correction $\sigma_{xc}-\sigma_{xc}^{\mathrm{LDA}}$ to the LDA surface exchange-correlation energy $\sigma_{xc}^{\mathrm{LDA}}$, given by wave-vector interpolation (solid curve) and by the first gradient correction (dashed curve), as a function of the linear-potential parameter y_F. Heavy dots indicate the exact values (Refs. 9 and 11) of $\sigma_{xc}-\sigma_{xc}^{\mathrm{LDA}}$ for the infinite-square-barrier model $y_F=0$. Vertical lines indicate the "physical" density profiles found by energy minimization in the LDA. (Dotted curve: $\frac{1}{10}\sigma_{xc}^{\mathrm{LDA}}$ in RPA). The gradient correction at $r_s=6$ is included for completeness, but should be regarded cautiously, as it involves integrals over B_{xc} at rather large local r_s.

TABLE I. Results of energy minimization in RPA using the LDA Eq. (2), the wave-vector analysis (WV) Eq. (3), and the gradient expansion (GE) Eq. (4). r_s is the bulk density parameter, y_F the minimizing variable parameter in the linear potential, $\Delta\varphi$ the Coulomb dipole barrier in eV, and σ and σ_{xc} the jellium surface energy and exchange-correlation part thereof in ergs/cm^2.

r_s		y_F	$\Delta\varphi$	σ_{xc}	σ
2.07	LDA	3.25	5.53	2934	−534
	WV	3.23	5.49	3089	−367
	GE	3.39	5.86	3355	−192
4	LDA	1.33	1.12	284	176
	WV	1.29	1.09	302	197
	GE	1.54	1.27	346	223
6	LDA	0.64	0.45	73	67
	WV	0.62	0.44	79	73
	GE	0.73	0.48	86	78

TABLE II. Results of self-consistent calculations in RPA for the quantities in Table I. For the LDA and GE approximations, we have included the functional derivatives of Eqs. (2) and (4) in the self-consistent one-electron potentials, while for the WV approximation we have used the LDA self-consistent profiles, as justified in the text. (Unlike the linear-potential calculations, these calculations employed an analytic parametrization of the RPA, which may have overestimated σ_{xc} by ~15 ergs/cm^2 at $r_s = 2.07$ and ~2 ergs/cm^2 at $r_s = 6$.)

r_s		$\Delta\varphi$	σ_{xc}	σ
2.07	LDA	5.99	2995	−555
	WV	5.99	3153	−397
	GE	6.26	3416	−217
4	LDA	0.81	266	175
	WV	0.81	285	194
	GE	0.90	330	223
6	LDA	−0.01	54	63
	WV	−0.01	58	68
	GE	0.02	71	75

Note first that the wave-vector–analysis correction essentially agrees[9] with the exact correction[11,9] at $y_F = 0$, and with the gradient correction for $y_F \approx 8$, where the accuracy of the latter cannot be doubted. The gradient correction on the other hand is in serious error (too large by a factor of ~4) at y_F near zero, as was shown by previous calculations.[6] More importantly, at "physical" values of y_F indicated by vertical lines, the gradient correction is still too large by a factor of ~2. In other words, the density gradients must be much smaller than those of typical surfaces for the gradient expansion to work.

We now take view (b) of the linear potential and minimize the energy of a semi-infinite jellium with respect to y_F. In fact, this was how the vertical lines in Fig. 2 discussed earlier were determined. More important however is the information so obtained about the density profiles in the respective approximations of Eqs. (2)–(4). The results are shown in Table I, where the rather large differences in total surface energies among the various approximations are also shown. The profile-sensitive quantities are the Coulomb dipole barrier[2] $\Delta\varphi$ and y_F itself. Wave-vector analysis yields y_F's and $\Delta\varphi$'s almost identical to the LDA values, suggesting that the LDA profile is a good one; this could have been anticipated directly from Fig. 2, because the wave-vector correction to the LDA energy depends so weakly on the profile. On the other hand, the gradient correction predicts rather large (10–20%) changes in these quantities (and these changes in $\Delta\varphi$ found variationally in Table I are close to those we have found in fully self-consistent calculations; see Table II). Our previous arguments suggest that this large a correction to the density profile is spurious.

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[14] In Ref. 3 B_{XC} is obtained from calculation of the energy in RPA; this is therefore the appropriate choice to compare with wave-vector analysis in RPA. In Ref. 5 B_{XC} is obtained from expansion of the dielectric function $\epsilon(Q)$; B_{XC} so obtained is *very* sensitive to choice of $\epsilon(Q)$ [cf. D. J. W. Geldart, M. Rasolt, and R. Taylor, Solid State Commun. 10, 279 (1972)], and does not correspond to any well-defined approximation such as RPA for the energy. In Ref. 5 a coefficient is also found for the *next*-order gradient correction from $\epsilon(Q)$, but this method neglects contributions in the same order ∇^4 of unknown size which arise in nonlinear response.

Valence Band Structure of PbS from Angle-Resolved Photoemission

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The angular dependence of uv- (21.2-eV photon energy) induced photoemission from single-crystal PbS has been investigated. The dependence of the positions of observed peaks on $\vec{k}_\parallel$ is compared with the prediction of band-structure calculations. Nearly perfect agreement between theory and experiment is found by assuming that only peaks in the appropriate one-dimensional density of initial states calculated along lines of fixed $\vec{k}_\parallel$ contribute to the observed spectra.

The interpretation of angle-resolved photoelectron spectra (ARPES) in terms of electronic band structures suffers from the lack of information about the normal wave-vector component $k_\perp$ of the photoexcited electron inside the crystal. Therefore, nearly all recent ARPES experiments[1] have been confined to layer compounds with $k_\perp$ fixed in the direction normal to the layers; for such compounds, little or no energy dispersion is expected along $k_\perp$. Only a few exceptions[2] deal with "three-dimensional" crystals, and no straightforward and satisfying interpretation of the results has been given so far. In this Letter, we report the first ARPES measurements of PbS, which has the rock salt structure and a reasonably well-known band structure.[3,4] The positions of the peaks observed in the energy distribution spectra plotted versus the wave-vector component parallel to the crystal surface, $\vec{k}_\parallel$, can be understood almost completely in terms of the one-dimensional density of states calculated along lines defined by $\vec{k}_\parallel = \text{const}$ in reciprocal space.

The experiments were performed in a commercially available photoemission spectrometer described elsewhere.[5] The hemispherical electron analyzer was operated at a pass energy of 10 eV corresponding to a resolution of approximately 0.3 eV. The opening angle of the acceptance cone was 3°. A PbS single crystal was cleaved in vacuum along a (100) plane, the base pressure being less than 1×10^{-10} Torr. Immediately after cleaving, the resulting surface was analyzed *in situ* by means of low-energy electron diffraction (LEED). Nearly the whole cleavage plane with an area of approximately 10 mm^2 exhibited the square LEED pattern of a perfect (100) surface of a face-centered cubic crystal. No evidence for surface disorder or surface reconstruction could be detected. The diffraction pattern preserved its sharpness for at least 48 h under ultrahigh-vacuum conditions. No changes were observed in the angle-resolved uv-induced photoemission spectra during this time either, confirming that the surface remained free of contaminants.

The orientation of the crystal was established inside the ultrahigh-vacuum chamber by means of its LEED pattern. The configuration used in the ARPES measurements described here was as follows: Designating the surface normal as the [100] direction, the electron acceptance cone was chosen to lie in the (010) plane. Consequently, the projection $\vec{k}_\parallel$ of the electron momentum onto the surface was parallel to the [001] direction. All spectra were taken using the He I (21.2 eV) photons emitted by a differentially pumped resonance lamp. The incidence angle of the light, θ_ω, was kept constant at 45° whereas the electron acceptance direction varied from $\theta = -28.5°$ to $\theta = +21.0°$ in steps of mostly 1.5° (all angles refer to the surface normal).

In Fig. 1 we present some selected ARPES