Study of the density gradient expansion for the kinetic energy*

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The density-gradient expansion for the kinetic energy is studied by application of the expansion to an inhomogeneous system of noninteracting fermions, and its convergence demonstrated. The inhomogeneity in the density is created by assuming the electrons move in an effective potential which is linear in the positive half space and constant elsewhere. It is shown that the original von Weisäcker coefficient of the first density-gradient correction is inappropriate for both rapidly and slowly varying densities. The coefficient reduced by a factor of 9, however, is appropriate for all density profiles provided that the second density-gradient correction is included for the rapidly varying case. The applicability of the expansion to the metal-surface problem is discussed, and the inclusion of the second density-gradient correction with its nonlinear response contributions shown to be of major significance in such calculations. A semiempirically determined value of 1.336 for the coefficient of the second gradient correction which leads to results which are essentially exact over a wide range of density profiles including the metallic range is proposed.

In the density-functional formalism of Hohenberg and Kohn,[1] the ground state of an interacting inhomogeneous electron gas in a static external potential is written as a functional of the density. One of the difficulties of the Hohenberg-Kohn theorem is the construction of an appropriate functional representing the kinetic energy. Employing the Hohenberg-Kohn formalism, Kohn and Sham[2] have shown that it is possible to obtain the exact ground-state energy of the system by solving self-consistently a set of single-particle Schrödinger-like equations, provided the exact exchange and correlation energy functional of the density is known. In essence they treat the kinetic energy as a functional of the density of a noninteracting electron gas. The set of single-particle equations to be solved for the N-particle system is

$$[-\tfrac{1}{2}\nabla^2 + V(\rho(\vec{r}))]\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \tag{1}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N} \psi_i^*(\vec{r})\psi_i(\vec{r}), \tag{2}$$

where $\rho(\vec{r})$ is the density and $V(\rho(\vec{r}))$ is the effective potential in which the particles move, being the sum of the electrostatic and exchange-correlation contributions which are themselves dependent on the density. The exact exchange-correlation energy functional of the density is of course unknown and must be approximated. However, the kinetic energy $E_k(\rho(\vec{r}))$ within this self-consistent formalism can be treated exactly and is given as

$$E_k(\rho(\vec{r})) = \sum_{i=1}^{N} \epsilon_i - \int V(\rho(\vec{r}))\rho(\vec{r})\,d\vec{r}. \tag{3}$$

Thus within the density-functional formalism of Kohn and Sham, the kinetic energy (and all other

properties) are dependent on a knowledge of the single-particle wave functions $\psi_i(\vec{r})$.

There also exist variational formalisms[3-5] whereby the density of an inhomogeneous interacting electron gas may be obtained accurately without having to resort to the self-consistent solution of Schrödinger-like equations or the use of correlated wave functions. Employing only crude approximations to the exact wave function, these variational principles lead to results for the density correct to second order as is the case for the energy on application of the Rayleigh-Ritz variational principle.[6] A generalization of these variational principles to the single-particle density matrix[7] leads to accurate results not only for the density but also the momentum density.[8] Thus within such a formalism one obtains directly the density rather than single-particle wave functions from which the density is obtained. In order to determine the kinetic energy one therefore has to resort[9] to the density gradient expansion for this property. Of course, it is also possible to employ this gradient expansion by using trial wave functions or parametrized analytic forms for the density. The latter approach has been employed for the variational determination of metal surface energies[10-12] in the jellium approximation and the results are observed to lie considerably below those of the self-consistent calculations of Lang and Kohn.[13] We have also recently applied[14] the variational principles mentioned above to the determination of the density at metallic surfaces correct to second order. Thus we are interested in studying the convergence properties of the kinetic-energy density-gradient expansion and in particular

to arrive at conclusions regarding its accuracy for the metal surface problem. In our study we therefore restrict ourselves to density profiles of the form that exist at metallic surfaces but which can be made to vary either rapidly (corresponding to low bulk densities) or very slowly (high bulk densities) in comparision with the local Fermi wavelength and screening length with the intermediate densities corresponding to those existing at metallic surfaces.

The density-gradient expansion for the kinetic-energy contribution to the surface energy of an inhomogeneous electron gas may be written as[15]

$$E_k^{GE}(\rho(\vec{r})) = E_k^{(1)}(\rho(\vec{r})) + E_k^{(2)}(\rho(\vec{r})) + E_k^{(3)}(\rho(\vec{r})), \tag{4}$$

where

$$E_k^{(1)}(\rho(\vec{r})) = \frac{3}{10}(3\pi^2)^{2/3} \int \rho(\vec{r})[\rho^{2/3}(\vec{r}) - \bar{\rho}^{2/3}] \, d\vec{r}, \tag{5}$$

$$E_k^{(2)}(\rho(\vec{r})) = \frac{\lambda}{8} \int \frac{|\vec{\nabla}\rho(\vec{r})|^2}{\rho(\vec{r})} \, d\vec{r}, \tag{6}$$

$$E_k^{(3)}(\rho(\vec{r})) = \frac{\gamma}{(3\pi^2)^{2/3}540} \int \rho(\vec{r})^{1/3}$$

$$\times \left[\left(\frac{\nabla^2\rho(\vec{r})}{\rho(\vec{r})}\right)^2 - \frac{9}{8}\left(\frac{\nabla^2\rho(\vec{r})}{\rho(\vec{r})}\right)\left(\frac{\vec{\nabla}\rho(\vec{r})}{\rho(\vec{r})}\right)^2 \right.$$

$$\left. + \frac{1}{3}\left(\frac{\vec{\nabla}\rho(\vec{r})}{\rho(\vec{r})}\right)^4\right] d\vec{r}. \tag{7}$$

In the above equations $E_k^{(1)}$ is the Thomas-Fermi (TF) contribution[16] to the surface kinetic energy with $\bar{\rho} = k_F^3/3\pi^2$ being the bulk density. In terms of the Wigner-Seitz radius r_s, the Fermi momentum $k_F = 1/\alpha r_s$, $\alpha^{-1} = (\frac{9}{4}\pi)^{1/3}$. With the coefficient $\lambda = 1$, $E_k^{(2)}$ is the first density-gradient correction originally proposed by von Weisäcker.[17] Subsequent rigorous derivations[18-21] of this first gradient correction valid for slowly varying densities have led to a value of the coefficient λ reduced by a factor of 9. With the total kinetic-energy density written as the sum of the TF plus first gradient correction, the Euler equation for the density is

$$\frac{(3\pi^2)^{2/3}}{2}[\rho(\vec{r})]^{2/3} + \frac{\lambda}{8}\left(\frac{\vec{\nabla}\rho(\vec{r})}{\rho(\vec{r})}\right)^2 - \frac{\lambda}{4}\frac{\nabla^2\rho(\vec{r})}{\rho(\vec{r})} + V(\vec{r}) = E, \tag{8}$$

where $V(\vec{r})$ is the potential in which the noninteracting particles move and E the Lagrange multiplier ensuring the conservation of the total number of particles. For the example of a weakly perturbed uniform system of noninteracting fermions it has been shown[22,23] from the above equation that the original von Weisäcker coefficient gives asymptotically exact results for short wavelength perturbations corresponding to rapidly varying densities, whereas $\lambda = \frac{1}{9}$ gives asymptotic-

ally exact results for the case of slowly varying densities. The von Weisäcker density does, however, lead to an upper bound for the energy.[24] For atomic systems[25] the von Weisäcker coefficient leads to good densities for the outer part of atoms as compared to those obtained quantum mechanically whereas a coefficient of $\lambda = \frac{1}{5}$ appears to be appropriate for interior densities. $E_k^{(3)}$ with the coefficient $\gamma = 1$ is the second density-gradient correction valid for slowly varying densities as obtained originally by Kirzhnits[19] and modified by Hodges.[26] The first term of $E_k^{(3)}$ is the linear response theory contribution to fourth order in the gradient operator. The last two terms arise from nonlinear response and their inclusion should shed light on the importance of such contributions to the metal surface problem.

The model-effective potential we use for the study of the kinetic-energy density-gradient expansion is the linear potential model[27,28] which has also recently been employed[29] to study the gradient expansion for the exchange-correlation energy of the inhomogeneous electron gas. The electron density is thus a function only of the coordinates of the direction of the inhomogeneity. The primary advantage of this model potential is that by adjusting the field strength it is possible to change the density from one which is extremely rapidly varying to one which is very slowly varying so that the gradient of the density can be physically changed for each point in space. A second principle advantage of this potential is that it leads to electronic densities in the metallic range (and hence to all metal surface properties[27,28]) which very closely approximate the self-consistently obtained values of Lang and Kohn,[13] particularly for medium- and high-density metals. Thus meaningful conclusions regarding the density-gradient expansion for the kinetic energy can be arrived at for the metal surface problem. A calculation in the step-potential model has recently been performed[30] but due to the limitations of this model[31,32] only trends with respect to the convergence of the gradient expansion can be observed. In addition this representation of the effective potential at a metal surface does not lead to accurate densities.

We assume the potential which gives rise to the inhomogeneous density profile to be

$$V(x) = Fx\Theta(x), \tag{9}$$

where F is the field strength. In terms of the slope parameter y_F, $F = \frac{1}{2}k_F^2/x_F$, $\frac{1}{2}k_F^2$ is the Fermi energy[15] and $\Theta(x)$ is the step function. The solution of the Schrödinger equation for this potential is

$$\psi_k(x) = \begin{cases} -(2/L)^{1/2}\sin[kx + \delta(k)] & \text{for } x \leq 0, \\ C_k \text{Ai}(\xi) & \text{for } x \geq 0, \end{cases} \tag{10}$$

where $\mathrm{Ai}(\zeta)$ is the Airy function, $\zeta=(x-E/F)(2F)^{1/3}$ and E is the energy. The normalization constant C_k and the phase shift $\delta(k)$ are determined by the requirement of the continuity of the wave function and its logarithmic derivative. Thus

$$C_k=-(2/L)^{1/2}\sin\delta(k,x_F)[\mathrm{Ai}(-\zeta_0)]^{-1} \tag{11}$$

and

$$\delta(k,x_F)=\cot^{-1}\left(\frac{1}{\sqrt{\zeta_0}}\frac{\mathrm{Ai}'(-\zeta_0)}{\mathrm{Ai}(-\zeta_0)}\right) , \tag{12}$$

where $\zeta_0=(k^2/k_F^2)(k_Fx_F)^{2/3}$ and where $\mathrm{Ai}'(\zeta)$ is the

derivative of the Airy function.

The electronic density per unit surface area is then

$$\rho(x)=\frac{L}{2\pi^2}\int_0^{k_F}(k_F^2-k^2)|\psi_k(x)|^2\,dk \tag{13}$$

and for purposes of overall charge neutrality we assume a uniform positive background of density $\rho_+=k_F^3/3\pi^2$ to end abruptly at $x=a$. With a change of variables to $y=k_Fx$ and $q=k/k_F$, the density and its first and second derivatives normalized with respect to the bulk density are

$$\frac{\rho(y)}{\bar\rho}=\begin{cases} 1-\dfrac{3}{2}\displaystyle\int_0^1 dq\,(1-q^2)\cos2[qy+\delta(q,y_F)] & \text{for } y\leqslant 0 , \\[2mm] 3y_F^{2/3}\displaystyle\int_0^1 dq\,\dfrac{(1-q^2)q^2}{\Lambda(q,y_F)}\,\mathrm{Ai}^2(\zeta) & \text{for } y\geqslant 0, \end{cases} \tag{14}$$

$$\frac{1}{\bar\rho}\frac{d\rho(y)}{dy}=\begin{cases} 3\displaystyle\int_0^1 dq\,(1-q^2)q\sin2[qy+\delta(q,y_F)] & \text{for } y\leqslant 0 , \\[2mm] 6y_F^{1/3}\displaystyle\int_0^1 dq\,\dfrac{(1-q^2)q^2}{\Lambda(q,y_F)}\,\mathrm{Ai}(\zeta)\,\mathrm{Ai}'(\zeta) & \text{for } y\geqslant 0, \end{cases} \tag{15}$$

$$\frac{1}{\bar\rho}\frac{d^2\rho(y)}{dy^2}=\begin{cases} 6\displaystyle\int_0^1 dq\,(1-q^2)q^2\cos2[qy+\delta(q,y_F)] & \text{for } y\leqslant 0 , \\[2mm] 6\displaystyle\int_0^1 dq\,\dfrac{(1-q^2)q^2}{\Lambda(q,y_F)}\,[\zeta\,\mathrm{Ai}^2(\zeta)+\mathrm{Ai}'^2(\zeta)] & \text{for } y\geqslant 0, \end{cases} \tag{16}$$

where $y_F=k_Fx_F$ is the slope parameter, $\zeta=(y-q^2y_F)y_F^{-1/3}$, $\zeta_0=q^2y_F^{2/3}$, and $\Lambda(q,y_F)=\zeta_0\mathrm{Ai}^2(-\zeta_0)+\mathrm{Ai}'^2(-\zeta_0)$. Note that the density and its derivatives as written in Eqs. (14)–(16) are universal functions of the slope parameter y_F. Large values of the slope parameter correspond to slowly varying densities whereas the $y_F=0$ limit represents the infinite potential barrier model corresponding to a very rapidly varying density. With these expressions for the density and its derivatives, we then obtain the various components of the density gradient expansion E_k^{GE} for the kinetic energy as given above.

For particles moving in the linear potential $V(x)$ of Eq. (9), the exact kinetic-energy contribution to the surface energy may be obtained[13,33] from Eq. (3) as

$$\frac{E_k}{k_F^4}=\frac{1}{160\pi}\left[1+\frac{80}{\pi}\left(\frac{3}{5}\int_0^1 q\delta(q,y_F)\,dq\right.\right.$$

$$\left.\left.-\int_0^1 q^3\delta(q,y_F)\,dq\right)\right]$$

$$-\frac{1}{k_F^5}\int_{-\infty}^{\infty}[V(\rho;y)-V(\rho;-\infty)]\rho(y)\,dy . \tag{17}$$

This expression may be further simplified by exploiting the equality of the phase-shift rule of Sugiyama[33,34] to the charge-neutrality condition whereby

$$\int_0^1 q\delta(q,y_F)\,dq$$

$$=-\frac{2}{15}y_F+\frac{y_F^{1/3}}{2}\int_0^1 dq\,\frac{(1-q^2)}{\Lambda(q,y_F)}\,\mathrm{Ai}(-\zeta_0)\,\mathrm{Ai}'(-\zeta_0) . \tag{18}$$

Furthermore, it can easily be shown that

$$\int_0^1 q^3\delta(q,y_F)\,dq$$

$$=-\frac{2}{21}y_F+\frac{y_F^{1/3}}{4}\int_0^1 dq\,\frac{(1-q^4)}{\Lambda(q,y_F)}\,\mathrm{Ai}(-\zeta_0)\,\mathrm{Ai}'(-\zeta_0) . \tag{19}$$

Thus Eq. (17) for the exact surface kinetic energy as a universal function of the slope parameter may be written as

$$\frac{E_k}{k_F^4} = \frac{1}{160\pi}\left(1 - \frac{64y_F}{35\pi} + \frac{4y_F^{1/3}}{3\pi} \int_0^1 dq\, \frac{(1-q^2)(3+5q^2)}{\Lambda(q,y_F)}\right.$$

$$\left. \times \mathrm{Ai}(-\zeta_0)\,\mathrm{Ai}'(-\zeta_0)\right)$$

(20)

In Fig. 1 we plot the variation of the universal functions of the exact kinetic energy E_k/k_F^4 together with those of the Thomas-Fermi (TF) term $E_k^{(1)}$ and the sum of $E_k^{(1)}$ plus the first gradient correction $E_k^{(2)}$ for both $\lambda=1$ and $\frac{1}{9}$ as a function of the slope parameter y_F. We also plot the universal function of the sum of all three terms of the gradient expansion E_k^{GE} with $\lambda=\frac{1}{9}$ and $\gamma=1$. Note that the origin of the abscissa in the figure is at $y_F = 0.5$. The graph demonstrates definitively the convergence of the gradient expansion E_k^{GE} as the density becomes more slowly varying. The percentage errors in the results for the TF, TF plus first gradient correction and TF plus first and second gradient corrections over this range of slope parameter are listed in Table I. Over the entire range of slope parameter considered, the Thomas-Fermi term may be observed to be a very poor approximation to the exact result even for slowly varying densities. At $y_F = 6$, this error is still 4%, whereas E_k^{GE} has converged to within 0.2% of the exact result. For rapidly varying densities, TF fails as anticipated being in error by 273% at $y_F = 0.5$. The addition of the first density-gradient correction improves results considerably becoming a better and better approximation as the density becomes more slowly varying. For example at $y_F = 1$, the addition of $E_k^{(2)}$ reduces an error of 86% in the TF result to 44%, and at $y_F = 6$ gives rise to a result within 0.8% of the exact value. As may be observed from column 4 of Table I, the inclusion of the second density gradient term to the series removes practically all error for $y_F \geq 2.0$. However, even for rapidly varying den-
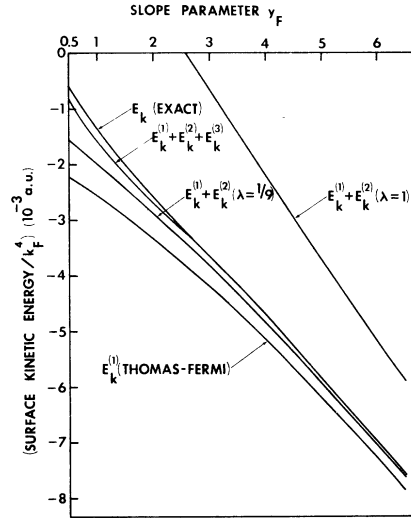

FIG. 1. Plot of the universal functions of the exact surface kinetic energy E_k/k_F^4 (denoted by E_k), and those of the Thomas-Fermi (TF) contribution $E_k^{(1)}$, TF plus first gradient correction $E_k^{(1)} + E_k^{(2)}$ ($\lambda=1$ and $\frac{1}{9}$), and TF plus first and second gradient corrections $E_k^{(1)} + E_k^{(2)}$ ($\lambda=\frac{1}{9}$) + $E_k^{(3)}$ ($\gamma=1$), as a function of the slope parameter y_F.

sities, this form of the second gradient term gives rise to substantial corrections in the appropriate direction. At $y_F = 1$, E_k^{GE} is in error by only 16%.

Having demonstrated the convergence of the density-gradient expansion for the kinetic energy, we next wish to understand how meaningful the application of such an expansion is for the metal surface problem. In order to do this we must develop a correspondence between a given bulk density and a specific density profile at the surface as produced by this model calculation. In other words, we must relate the slope parameter y_F which determines the density variation at the sur-

TABLE I. Percentage errors in (i) the Thomas-Fermi (TF) contribution $E_k^{(1)}$ to the surface kinetic energy, (ii) the sum of TF and first gradient correction $E_k^{(1)} + E_k^{(2)}$, and (iii) in the sum of TF and first and second gradient corrections $E_k^{GE} = E_k^{(1)} + E_k^{(2)} + E_k^{(3)}$.

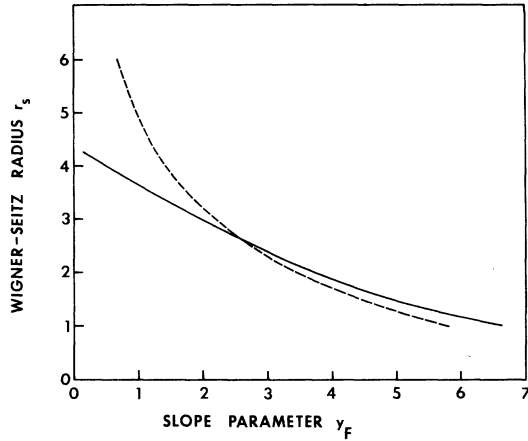| Slope parameter y_F	$E_k^{(1)}$ (Thomas-Fermi)	$E_k^{(1)} + E_k^{(2)}$ ($\lambda=\frac{1}{9}$)	E_k^{GE} ($\lambda=\frac{1}{9}$; $\gamma=1$)	E_k^{GE} ($\lambda=\frac{1}{9}$; $\gamma=1.336$)
0.5	273	161	41	0
1.0	86	44	16	6
1.5	46	20	7	3
2.0	30	11	4	1
3.0	15	4	1	0.1
4.0	9	2	0.4	0.2
5.0	6	1	0.3	0.05
6.0	4	0.8	0.2	0.01

FIG. 2. Full line is a plot of the correspondence between the Wigner-Seitz radius r_s and the slope parameter y_F as determined by the Budd-Vannimenus theorem. The dashed curve is the correspondence as determined by the variational principle for the energy.

face to the bulk density or equivalently, the Wigner-Seitz radius r_s defined as $\frac{4}{3}\pi r_s^3 = 1/\bar{p}$. One criterion we use is the Budd-Vannimenus theorem,[35,36] which relates the difference in electrostatic potential V_{es} between that at the metal surface and that in the bulk, to the energy per electron for the uniform electron gas. According to this theorem,

$$\Delta V = V_{es}(a) - V_{es}(-\infty) = \rho \frac{d\epsilon_T}{d\rho} , \qquad (21)$$

where ϵ_T is the sum of the kinetic, exchange, and correlation energies per particle for the uniform electron gas. Employing the Wigner interpolation formula[37] $\epsilon_c = -0.44/(r_s + 7.8)$ for the correlation energy per particle, we have ΔV in units of the free-electron Fermi energy to be

$$\Delta V = 0.4 - 0.0829 r_s - 0.0796 r_s^3/(r_s + 7.8)^2 . \qquad (22)$$

We obtain the difference ΔV for any arbitrary value of the slope parameter y_F by using the expression for V_{es} for this model potential given in Ref. 27, and the corresponding value for the bulk density from Eq. (22). A plot of this correspondence between y_F and r_s is given in Fig. 2. Another method by which we may relate the bulk density to the slope parameter is by application of the variational principle for the energy.[6] We write the surface energy as the sum of the kinetic, electrostatic, and the exchange-correlation energy as determined say in the local density approximation, and minimize the energy with respect to the slope parameter for a specific value of r_s. The results of the application of this criterion for the correspondence between r_s and y_F are also plotted in Fig. 2.

Note that in either case the surface density of metals (for which $2 \leqslant r_s \leqslant 6$) may be represented by values of the slope parameter in the range $0 \leqslant y_F \leqslant 4$. A study of both Figs. 1 and 2 thus indicates that the density-gradient series for the kinetic energy (with $\lambda = \frac{1}{9}$ and $\gamma = 1$) is an excellent approximation for high-density metals, reasonably good for medium densities, and poor for low-density metals. On the other hand, the sum of the TF plus first gradient correction with $\lambda = \frac{1}{9}$ leads to poor results over the entire metallic range being consistently well below the exact results. It is thus possible to understand why the surface-energy values of the statistical calculations of both Smith[11] and Paasch and Heitschold[12] lie considerably below those of the self-consistent calculations of Lang and Kohn.[13] These authors employed parameterized analytic forms for the density but included only the first density-gradient correction for the kinetic energy. They thus underestimated the kinetic energy considerably which in turn led to a lower value for the total surface energy. Thus if the statistical approach is to be employed for metal surface calculations it is imperative that the second density-gradient correction as given by Eq. (7) be included.

We have also plotted in Fig. 1 the variation of $E_k^{(1)} + E_k^{(2)}$ for the original von Weisäcker coefficient $\lambda = 1$. It is evident that the use of this coefficient leads to results for the kinetic energy which are in substantial error over the entire range of slope parameter considered in the figure, even having the wrong sign for $y_F \lesssim 2.5$. However, based on the work of Jones as discussed earlier, it is expected that the von Weisäcker coefficient should lead to convergence for the very rapidly varying limit. In order to see whether this is the case, we have extended our calculations to accurately determine the various components of the density-gradient expansion in the range $0 \leqslant y_F \leqslant 0.5$ and the results are plotted in Fig. 3. Note that $y_F = 0$ corresponds to the infinite barrier potential for which the density is most rapidly varying. A study of the figure indicates that even for rapidly varying densities the use of the von Weisäcker coefficient still leads to substantial errors and that even in the infinite barrier limit there is no indication of convergence. It does however have the right sign for $y_F \lesssim 0.25$. On the other hand, the use of $\lambda = \frac{1}{9}$ is still a better approximation for $y_F \gtrsim 0.25$ and the addition of the second density-gradient correction improves matters still further. Of course, for $y_F = 0$, $E_k^{(3)}$ diverges. It thus appears that for physical density profiles which are rapidly varying, the choice of $\lambda = \frac{1}{9}$ is still the correct one although one must add in the correction due to the second density-gradient term.
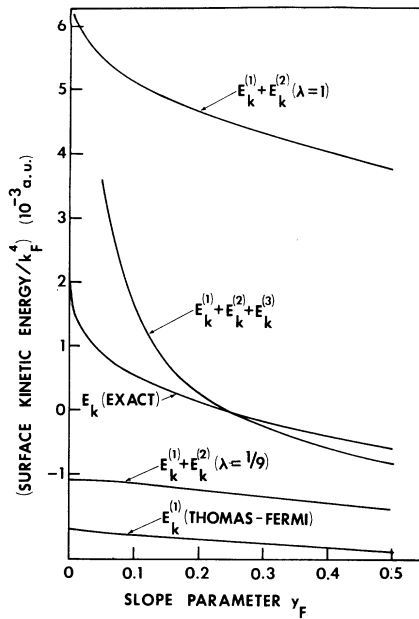
FIG. 3. Figure caption is the same as that of Fig. 1. The range of the slope parameter y_F considered, however, is different.
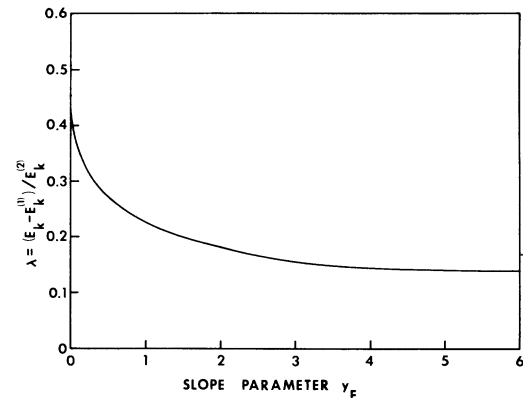

FIG. 4. Variation of the coefficient λ of the first gradient correction which leads to the exact result for the kinetic energy when only the first two terms of the expansion are considered, as a function of the slope parameter y_F.

An interesting question which thus arises is what value of λ would lead to the exact kinetic energy if only the Thomas-Fermi plus first density-gradient correction of the expansion were to be employed in the calculation. This is important since Eq. (8) has been solved in many applications in atomic and molecular physics and for the metal surface problem[38] (with $\lambda = \frac{1}{9}$). We have therefore plotted in Fig. 4 the variation of $\lambda = (E_k - E_k^{(1)})/E_k^{(2)}$ as a function of the slope parameter. The fact that there is a substantial variation in the values of λ thus obtained indicates that no one value of the coefficient will suffice over the entire range of densities considered. However, for a specific metal the correct value of λ to be used in Eq. (6) or in any parametrized density calculation can be obtained from this graph since there exist reliable criteria for the correspondence between the slope parameter and the Wigner-Seitz radius. An alternative approach would be to solve the Euler equation (8) in conjunction with the constraint of the Budd-Vannimenus theorem.

Finally we note that although the results of the density gradient expansion with $\lambda = \frac{1}{9}$ and $\gamma = 1$ are very accurate in the range of both metallic and higher densities, they still lie a few percent below the exact values. Thus to improve matters further, we propose the following semiemperical method for the determination of the coefficient γ of the second density-gradient correction. We adjust the coefficient γ such that the results of the grad-

ient expansion agree with the exact result at $y_F = 0.5$. This value of y_F corresponds to a very rapidly varying density for which there is a substantial error between the exact result and that of the original gradient expansion (See Table I). The value of γ thus obtained is 1.336. The results of using this coefficient for the second gradient correction are shown in Fig. 5, and the percentage errors are given in the last column of Table I. Note that the energy scale has been considerably expanded in this diagram. As may be observed, the improvement in the results over those shown
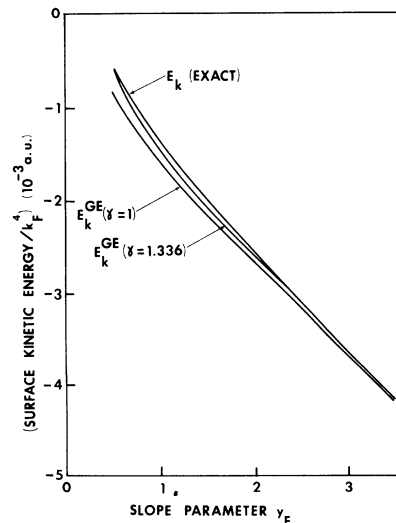

FIG. 5. Plot of the universal functions of the exact surface kinetic energy E_k/k_F^4 (denoted by E_k), and the energy as obtained by the gradient expansion E_k^{GE} for both $\gamma = 1$ and 1.336, as a function of the slope parameter y_F.

in Fig. 1 are substantial for all densities being in error by less than 3% for $y_F \geq 1.5$ and within 0.01% of the exact result at $y_F = 6$.

In conclusion we note that we have demonstrated the convergence of the density-gradient expansion for the kinetic energy for a semiinfinite system of noninteracting fermions confined at its surface by a linear potential. The value of $\frac{1}{9}$ for the coefficient of the first density-gradient expansion term is the appropriate choice for slowly varying densities in agreement with theoretical predictions, and should also be employed for rapidly varying densities such as those existing at metal surfaces, provided the second gradient correction is included. The choice of the original von Weisäcker coefficient, however, leads to results which are consistently in error for both rapidly and slowly varying densities. A semiemperically determined value of 1.336 for the coefficient of the second density-gradient term leads to results which are essentially exact over a very wide range of density profiles. Obviously, as shown above, the addition of this second density-gradient contribution with its nonlinear response terms is an important factor for convergence and particularly so for metal surface calculations. In Ref. 29 evidence was presented that indicated that the first density-gradient correction for the exchange-correlation energy was inappropriate for metallic surface densities. Thus together with the conclusions of this work, we expect the second density-gradient correction including its nonlinear response terms to be necessary components of any gradient expansion calculation of the exchange-correlation energy of metal surfaces. In order to better understand the applicability of this expansion to the metal surface problem we are presently investigating the gradient expansion for screened Coulomb exchange within this model potential, (thus ensuring the use of physically realistic densities) and in addition are studying means of treating the screening locally in our calculations.

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