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Exact solution of approximate density functionals for the kinetic energy of the electron gas

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We study the metal-surface jellium model with different approximations for the kinetic-energy density-functional model including the gradient expansions and other fully nonlocal functional models. Instead of the approximated variational method used in the previous analysis of the problem, we get the exact (numerical) solution with a modified conjugated-gradient technique, which leads to important differences in the surface energy, work function, and electronic profiles.

The density-functional formalism (DFF) of Hohenberg, Kohn, and Sham[1] allows one to study electronic systems in terms of the total electronic density distribution, $n(r)$, without reference to the N-body wave function. The total energy of a many-electron system is written as a functional of $n(\mathbf{r})$, with three different contributions:

$$E[n(\mathbf{r})]=T[n(\mathbf{r})]+E_h[n(\mathbf{r})]+E_{\mathrm{xc}}[n(\mathbf{r})] , \qquad (1)$$

where E_h represents the Hartree energy which includes the Coulomb interactions between the electrons and with the ions, E_{xc} is the exchange and correlation energy for which we may use several approximated forms, like the simplest local-density approximations (LDA) or other nonlocal functional models.[3] Finally, T is defined as the kinetic-energy functional for a system of noninteracting electrons. Unfortunately, there is not an exact explicit form for $T[n]$, although it is given in an implicit way by the solutions of the one-electron Schrödinger equation. However, this is a step backwards from the original aim of the DFF of having a description of the system in terms of $n(\mathbf{r})$. There have been several attempts to find a good explicit form to approximate $T[n]$. The Thomas-Fermi approximation[4] may be considered as the precursor of these attempts, having come long before the basis of the DFF was laid. In that approach, the kinetic energy is evaluated as if the system were made of pieces of homogeneous density, so that the kinetic energy per electron at each point is evaluated with the function $t(n)$ which would give the kinetic energy per electron in a homogeneous system of density n. The Thomas-Fermi density functional $T_{\mathrm{TF}}[n(\mathbf{r})]$ will only give an accurate description of $T[n]$ if $n(\mathbf{r})$ changes very smoothly in the scale of the inverse of the Fermi wave vector k_F, which is not true for the usual systems of interest: atoms, molecules, and solids.

The next step from the Thomas-Fermi approximation will be a gradient expansion[4] in which $T[n]$ is developed in series of $\nabla n(\mathbf{r})$, the first contribution goes with the square of $\nabla n(\mathbf{r})$ as

$$T[n(\mathbf{r})]=T_{\mathrm{TF}}[n(\mathbf{r})]+\tfrac{1}{72}\int \frac{[\nabla n(\mathbf{r})]^2}{n(\mathbf{r})}d\mathbf{r} \qquad (2)$$

in atomic units. We call this approximation "GE2" hereafter. It is interesting to recall that the exact form of $T[n]$ for a one-electron system has the same form as that of the second term in (2), without any local contribution, but with an extra factor of 9. This is called the Weizsacker term[5] and should be exact in the regions with very low electron density. The gradient expansion may be taken up to four order,[6] (we call it "GE4" hereafter), but it cannot be pushed further because higher-order terms will produce divergences in the regions of vanishing density.[7] There have been several attempts to derive a density functional for $T[n]$ avoiding the problems of the gradient expansion.[8,9] We will refer here to the work of Chacón *et al.*[9] using a fully nonlocal description of $T[n]$, in particular we refer hereafter to the Chacón-Alvarellos-Tarazona (CAT) approximation to the functional model called "T_2" in Ref. 9, which seems to be the most promising. A basic problem to which all these approximations have been applied is the metal surface in the jellium model, so that the density distributions of electrons, $n(z)$, depends only on the distance to the surface z. The problem was studied by Lang and Kohn[10] (LK) with the LDA for the exchange and correlation energy and the exact treatment of the kinetic energy, i.e., by solving the one-electron Schrödinger equation, so that it became a good test for any approximate model of $T[n]$, which would, of course, require a much little computational effort. However, all the previous studies with approximate functionals for $T[n]$, beyond Thomas-Fermi,[9,11-13] were done with variational approximations, so that the minimization of $E[n]$ was restricted to a family of density profiles with a few parameters, the simplest and most frequent one being the exponential profile with a single parameter to vary the width of the interface.[11,12] Broader parametric families have also been used,[9,13] but it was always uncertain what were the true characteristics of the functional approximation and what was coming from the restricted variational solution.

What we present here is the exact (numerical) solution of the problem for the different approximate models of $T[n]$. We have used the conjugate-gradient method,[14] in which starting from a given initial guess for the density profile $n(z)$, we move in the functional space with the

TABLE I. Surface energies and work functions in the range of metallic densities. In parentheses one the values obtained with the variational method using the exponential parametrization for the density profile. In this case Φ has been calculated using the Koopmans theorem.

	Surface energy (ergs/cm^2)				Work function (eV)			
r_s	GE2[a]	GE4[b]	CAT[c]	LK[d]	GE2[a]	GE4[b]	CAT[c]	LK[d]
2	−1188	−1090	−1077	−1008	3.07	3.54	3.45	3.89
	(−1144)	(−982)			(3.67)	(4.40)		
3	101.8	153	166	199	2.85	3.24	3.38	3.50
	(118)	(202)			(3.19)	(4.00)		
4	102.2	132	143	158	2.60	2.89	2.98	3.06
	(110)	(162)			(2.93)	(3.64)		
5	61.6	81	88	98	2.37	2.60	2.63	2.73
	(68)	(102)			(2.75)	(3.32)		
6	36.2	50	53	60	2.18	2.35	2.38	2.41
	(42)	(65)			(2.58)	(3.03)		

[a] References 4 and 11.
[b] References 6 and 12.
[c] Reference 9.
[d] Reference 10.

direction of the functional gradient $\delta E/\delta n(z)$ orthogonalized to the directions previously tried. This is equivalent to numerically solving the Euler equation for the exact functional minimum of $E[n]$, so that we do not depend on any parametrized family of variational functions. We do not give a description of the method, which may be found in Ref. 14, but it is worthwhile to point out that the main difficulty in its application to our problem is the requirement of charge neutrality, which any physical solution should have. This is imposed by means of a Lagrange multiplier, but this makes the whole method less efficient. In particular, it becomes very cumbersome for the GE4 functional, because of the high-order powers of $n(z)$ in the denominator of the fourth-order gradient coefficient, which makes it extremely nonlinear in the region of vanishing $n(z)$, outside the metal, so that many conjugate-gradient iterations are required.

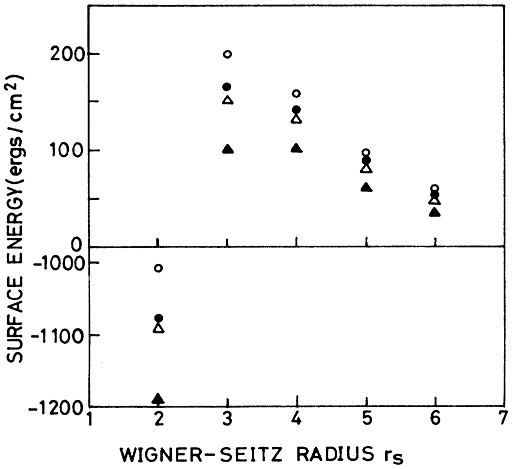

FIG. 1. Surface free energy σ for values of r_s in the range of metallic densities, as given by different treatments of $T[n(r)]$. Open circles, exact (LK) results; solid circles, CAT; open triangles, GE4; solid triangles, GE2.

We first comment on the results for the surface energy σ. The results attained by Smith[11] with the GE2 using the simple exponential parametrization were too low compared with the exact LK results and they become worse as the variational trial function is improved. The final surface energies which our exact minimization gives for this functional are much lower than the exact (LK) results (see Table I and Fig. 1). For the next-order gradient expansion, GE4, the surface energy obtained with the exponential density profile[12] was above the LK results (by a few percent), so that one may hope that, by improving the variational calculation, the true minimum value of σ would be closer to the exact (LK) values. However, the exact minimization makes σ decrease too much, to final values again below the exact values, but closer to them than with the GE2. The results of σ with the CAT functional model do not present strong changes with respect to the five-parameter variational calculation presented in the original work.[9] The final surface energies are also below the exact values (see Table I and Fig. 1) but the discrepancy is about a half of that for GE4.

Another quantity of interest in this system is the work function Φ, i.e., the work required to extract an electron from the metal through the surface. There are two different ways to calculate Φ, the first one being the direct evaluation in terms of the surface dipole and the chemical potential using the Koopmans theorem:[4]

$$\Phi=\Delta\phi-\mu \, , \tag{3}$$

where $\Delta\phi$ is the surface-dipole barrier and μ is the total chemical potential of the uniform electron gas, $\mu=d[n\varepsilon(n)]/dn$, in terms of the total energy per electron, $\varepsilon(n)$. The second way to get Φ is the "displaced-profile charge in self-consistent field" (DPΔSCF) method[4,15] which relates Φ to the difference in electrostatic potential from the bulk, $\phi(\infty)$, to the edge of the neutralizing background, $\phi(0)$:

$$\Phi=\phi(\infty)-\phi(0)-\varepsilon(n) \, . \tag{4}$$

In a full minimization, as we present here, both results should agree (we have used this as an additional test for the convergence of our process), but in a partial variational minimization there may be a large difference between the two values of Φ. It has been argued[15] that in that case, (4) should provided a better guess to the true work function, and this is confirmed by our results. In Fig. 2 and in Table I we present the results for Φ with the different approximate functionals together with the exact LK values. It is worthwhile to remark that the good agreement for the Koopmans values of Φ for $r_s=4$ and 5 with GE2 and the exponential parametrization[12] was fortuitous; the final density distribution for that functional gives too low self-consistent values of the work function. The final results with GE4 are better, but the nonlocal CAT functional is again the best.

Finally, we present in Fig. 3 the electronic density distribution for a bulk Wigner-Seitz radius $r_s=6$. The exact (LK) profile shows a maximum of about 1.15 times the bulk density, followed by the Friedel oscillations, with period $1/2k_F$, which reflects the logarithmic divergence of the Lindhard response function. That singularity is eliminated by any truncated Taylor series around $k=0$, so that the oscillating tail in $n(z)$ is missing in the GE2 and GE4 approximations.[4] In both cases there is a single maximum of $n(z)$ lower than in the exact result: for GE2 it is 1.12 times the bulk density and for GE4 it is even lower. Our fully minimized result with GE4 is very similar to that with the five-parameter variational parameters given in Ref. 9 and to the recent work of Orosz[12] using harmonic-oscillator functions (this latter does not give any value of σ or Φ). However, for the CAT functional we get important changes in the density profile with respect to the results with the five-parameter variational calculation.[9] The height and position of the first maximum of $n(z)$ are in excellent agreement with the exact LK result, and we also get the oscillating tail which is missing in the gradient expansion approximations. This could be expected because the CAT density functional is precisely constructed to reproduce the full response function of the bulk system, including the logarithmic divergence at $k=2k_F$. However, the use of the parametrized weight function proposed in the original work[9] as a simplification for the numerical calculations affects this feature, so that the agreement becomes worse beyond the second maximum. Probably this would be further improved if the CAT functional were used with the exact weight function. For lower values of r_s, the density profiles are smoother and the differences between the approximate and the exact LK results are smaller, but in keeping with the general trends of the $r_s=6$ case.

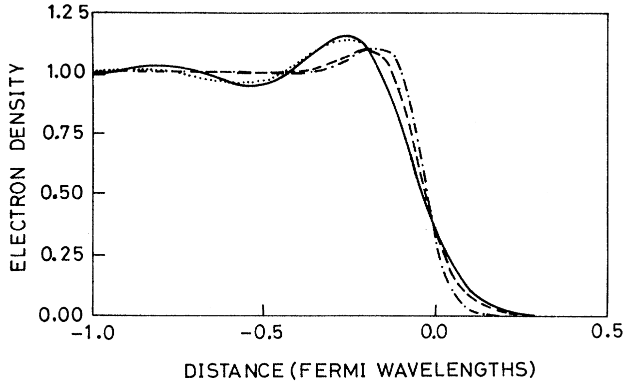

FIG. 3. Electronic density profile $n(z)$ at the jellium surface for $r_s=6$. Solid line, exact (LK) result; dashed line, GE2; dash-dotted line, GE4; dotted line CAT; this latter is very close to the solid line for points outside the metal.

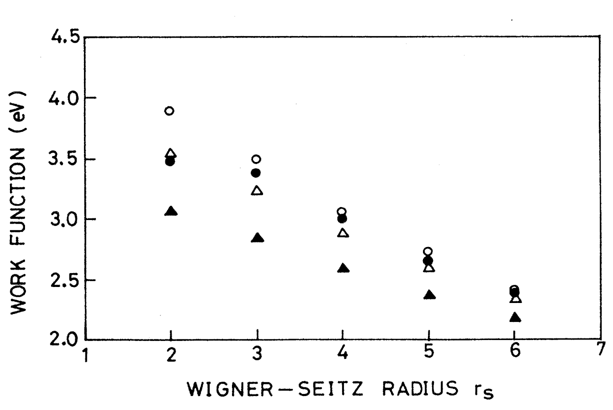

FIG. 2. Work function Φ for values of r_s in the range of metallic densities. The symbols are as in Fig. 2.

Another point of interest with respect to the density profile is the decay outside the interface, far from the metal. The exact solution of the Schrödinger equation gives an exponential decay, $n(z)\propto\exp(-Az)$, with a decay constant A, which is exactly the same given by the Weizsacker term in $T[n]$. However, GE2 contains only $\frac{1}{9}$ of this contribution, so that the exponential decay is too fast. The inclusion of the fourth-order term makes it even worse because, as may be easily verified, it is incompatible with an exponential decay. Unfortunately, the extremely nonlinear behavior of the density gradients with this approximation makes it very difficult to numerically analyze the true asymptotic decay of $n(z)$; for intermediate distances the electronic density for this approximation lies in between the GE2 and the exact LK results. The CAT functional contains as a basic ingredient the Weizsacker term with the correct factor, so we may expect it to give the exact exponential decay of $n(z)$. However, there is a small difference due to the scaling of the weight function in terms of the local density, which originates that a point outside the metal samples its environment far enough to get a contribution from the bulk. Nevertheless, this effect is not very important and in practice the decay of $n(z)$ with this functional is indistinguishable from the exact one (Fig. 3).

Summarizing, the CAT model for the kinetic energy of electron systems seems to be the best existing form for an explicit density functional for $T[n]$, and the conjugated-gradient method provides a useful way to handle it. The gradient-expansion approximations GE2 and GE4 give poorer results when fully minimized, and GE4 is particularly cumbersome to use with our method.

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