Comment on the theory of work function

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A new formula is derived for calculating the work function of jellium. A theorem is proved which shows that this new formula is equivalent to traditional methods, e.g., as given by Lang and Kohn. The new formula shows that the work function is related to the ground-state energy per particle. In addition we comment on a theorem recently proved by Budd and Vannimenus that allows the generalization of our formal result to an exact treatment of jellium; i.e., a treatment in which the exchange correlation energy functional is *not* approximated by a local density expression.

The modern theory of the work function of metals was formulated by Bardeen in 1936.[1,2] For the alkali metals, he calculated the contributions from the kinetic, exchange, and correlation energies, and discussed the surface dipole term. This latter contribution was calculated recently by Smith,[3] and much more accurately by Lang and Kohn,[4] and good agreement is obtained between theory and experiment. In essence these calculations are trying to determine the absolute magnitude of the energy of an electron on the Fermi surface of the metal.

We will show that the work function may also be computed as the ground-state energy per electron, with an additional term to account for the surface dipole. Of course, the ground-state energy is not the energy of an electron at the Fermi surface, but is an average over all of the electrons. We will show, for the jellium model of a metal, that this new definition is numerically and analytically identical to the conventional one.

To develop the equivalence of the two algorithms for the work function we first briefly summarize their derivations. A general definition of the work function Φ at zero temperature is

$$\Phi = [\varphi(\infty) + E_{N-1}] - E_N , \qquad (1)$$

where $\varphi(\infty)$ is the electrostatic potential energy of an electron at $x = +\infty$, while E_N and E_{N-1} are, respectively, the ground-state energies of the N (neutral) and $N-1$ electron metal. Since we limit ourselves to a jellium model, we presume a uniform positive background of charge exists in the region $x < 0$. The total charge in this background is chosen to neutralize that of N electrons. The difference between the two formal expressions for the work function obtained below arises from different prescriptions for the evaluation of the change of the ground-state energy of the metal upon the removal of one electron.

Lang and Kohn[4] remark that by thermodynamic definition

$$\mu = E_N - E_{N-1} , \qquad (2)$$

where μ is the chemical potential. Using the energy functional formalism, they next prove that

$$\mu = \frac{\delta E[n]}{\delta n(\vec{r})} \qquad (3)$$

if $E[n]$ is the exact electron energy functional. We refer the reader to the original paper for a formal definition and existence proof of this quantity.[5,6] Note that the derivative implied in (3) is a functional derivative with respect to electron density $n(\vec{r})$ but that the result is independent of $\vec{r}$. Lang and Kohn exploit this independence to evaluate $\delta E[n]/\delta n(\vec{r})$. Their argument is to consider an infinite uniform medium (all surfaces infinitely distant) and to note that the energy of such a system can be approximately written as

$$E = \int d\vec{r}\, n(\vec{r})$$
$$\times \left[\epsilon(n(\vec{r})) + v(\vec{r}) + \frac{e^2}{2} \int \frac{d\vec{r}'\, n(\vec{r}')}{|\vec{r} - \vec{r}'|} \right] + \overline{E} , \qquad (4)$$

where

$$\epsilon(n(\vec{r})) = \tfrac{3}{5} E_{KE} + \tfrac{3}{4} E_x + E_c , \qquad (5)$$

with

$$E_{KE} = \frac{\hbar^2 k_F^2}{2m} = E_F = \frac{3.68}{r_s^2} \frac{e^2}{2a_0} , \qquad (6)$$

$$E_x = -\frac{e^2}{\pi} k_F = -\frac{1.22}{r_s} \frac{e^2}{2a_0} , \qquad (7)$$

$$E_c = \frac{-0.88}{r_s + 7.8} \frac{e^2}{2a_0} , \qquad (8)$$

and $v(\vec{r})$ is the potential energy resulting from the positive background and a single electron while $\overline{E}$ is the potential energy of the background interacting with itself. The parameter r_s is determined by the electron density: $1/n(r) = \tfrac{4}{3} \pi (r_s a_0)^3$, with a_0 the Bohr radius. This decomposition nicely separates kinetic, exchange, correlation, and electrostatic energies. Lang and Kohn next make the reasonable ansatz that the $\delta E[n]/\delta n(\vec{r})$ of Eq. (3) for $\vec{r}$ deep

within a semi-infinite metal may be determined by taking the functional derivative of Eq. (4). Differentiating only the explicit density dependence there, they find that (3) becomes

$$\mu = E_{KE} + E_x + E_c' + \varphi^b(\vec{r}) \ , \tag{9}$$

where

$$E_c' = \frac{\partial}{\partial n} (n E_c) = -0.88 \frac{7.8 + \frac{4}{3} r_s}{(7.8 + r_s)^2} \frac{e^2}{2a_0} \tag{10}$$

and

$$\varphi^b(\vec{r}) = v(\vec{r}) + e^2 \int \frac{n(r')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$
$$= \varphi(-\infty) \ . \tag{11}$$

In the second line of (11) we have replaced the electrostatic potential energy of an electron in the infinite bulk metal (φ^b) by its electrostatic potential energy deep within a semi-infinite metal $[\varphi(-\infty)]$. Combining, we obtain the final result of Lang and Kohn for this jellium model:

$$\Phi = [\varphi(\infty) - \varphi(-\infty)] - (E_{KE} + E_x + E_c') \ , \tag{12}$$

where the last three terms are to be evaluated at the uniform density of the interior. A more explicit expression for the surface dipole term can be written using the net charge density of the system

$$\varphi(x) - \varphi(-\infty) = 4\pi e^2 \int_{-\infty}^{x} dx' \ (x' - x) f(x') \ , \tag{13}$$

so that since the system is neutral

$$\varphi(\infty) = \varphi(-\infty) = 4\pi e^2 \int_{-\infty}^{\infty} dx \, x f(x) \ . \tag{14}$$

Here $f(x) = n(x) - n_0 \theta(-x)$, where we note that the density depends only on x and $n_0[= n(x = -\infty)]$ is its value deep inside the metal.

Our new formula for the work function may be derived by making an alternate estimate of $E_N - E_{N-1}$. We begin by supposing that we may use Eq. (4) to compute the ground-state energy of even the semi-infinite metal. Then the difference in energy of the N and $N-1$ electron ground states is

$$E_N - E_{N-1} = \int d\vec{r} \, n_\sigma(\vec{r}) \left(\frac{\partial}{\partial n} (n\epsilon) + \varphi(\vec{r}) \right) \ , \tag{15}$$

where $n_\sigma(\vec{r})$ is the infinitesimal change in the density between the two ground states and is normalized to unity:

$$\int n_\sigma(\vec{r}) d\vec{r} = 1 \ . \tag{16}$$

We next pick a particular form for $n_\sigma(\vec{r})$. For a semi-infinite sample of surface area A we take

$$n_\sigma(\vec{r}) = -\frac{1}{n_0 A} \frac{dn}{dx} \ . \tag{17}$$

There is a simple physical reason for this choice. After the removal of one electron, the electron density readjusts so that it has the same average charge density deep inside the metal as before. Hence the actual change in charge density is located on the surface. The simplest model is where the charge density just contracts a bit. So if it has the density profile $n(\vec{r})$ before the electron is removed, it has the profile $n(\vec{r} - \hat{x} \delta x)$ after. Thus the change is

$$n_\sigma(\vec{r}) = n(\vec{r} - \hat{x} \, \delta x) - n(\vec{r}) \simeq -\delta x \frac{dn}{dx} \ . \tag{18}$$

The normalization condition (16) uniquely fixes $\delta x = (n_0 A)^{-1}$ and higher derivatives in (18) may be omitted because of their dependence upon higher inverse powers of $n_0 A$. Now if we put (18) into (15) we find

$$E_N - E_{N-1} = \int d\vec{r} \left(-\frac{1}{n_0 A} \frac{dn}{dx} \right) \left[\frac{d}{dn} (n\epsilon) + \varphi \right] = -\frac{1}{n_0} [n(x)\epsilon(x)]_{-\infty}^{\infty} + \int_{-\infty}^{\infty} dx \left(-\frac{1}{n_0} \frac{dn(x)}{dx} \right) \varphi(x) \ . \tag{19}$$

The terms from the upper limit of the first integral vanish since the density vanishes far outside the metal. The terms from the lower limit yield $\epsilon(x = -\infty)$. The second integral in (19) requires a bit more effort. In the Appendix it is shown that this contribution is given by

$$\int_{-\infty}^{\infty} dx \left(-\frac{1}{n_0} \frac{dn(x)}{dx} \right) \varphi(x) = \varphi(x = 0) \ . \tag{20}$$

So we derive for the work function the new formula

$$\Phi = [\varphi(\infty) - \varphi(0)] - (\tfrac{3}{5} E_{KE} + \tfrac{3}{4} E_x + E_c) \ , \tag{21}$$

where as in (12) the last three terms are to be

evaluated at the uniform density of the interior n_0.

It is interesting to compare the new result (21) with the conventional formula (12). Both contain the same sort of energy contributions, but in each case the coefficient is different and the surface dipole contribution is evaluated at a different point. The two formulas, however, seem to be numerically equal. Table I shows the work function calculated with each formula at three different densities. The first part of the table is just reproduced from Lang and Kohn.[4] Using computer results for $n(x)$ graciously supplied to us by Dr. N. D. Lang, we computed $\varphi(0)$ from Eq. (13) and verified the nu-

TABLE I. Work function of jellium in units of electron volts. The same result is obtained for both Eqs. (12) and (21). The one digit discrepancy of $r_s = 6$ is probably caused by slight errors in $\varphi(0)$.

r_s	Kinetic	Exchange	Correlation	Surface dipole	Work function
	$\dfrac{3.68}{r_s^2}$	$-\dfrac{1.22}{r_s}$	$\dfrac{0.88(7.8+\frac{4}{3}r_s)}{(7.8+r_s)^2}$	$\varphi(\infty)-\varphi(-\infty)$	Φ
2	12.52	-8.31	-1.30	$+6.80$	3.89
4	3.13	-4.15	-1.13	$+0.92$	3.07
6	1.39	-2.77	-0.99	$+0.04$	2.41
	$\dfrac{2.21}{r_s^2}$	$-\dfrac{0.916}{r_s}$	$\dfrac{0.88}{7.8+r_s}$	$\varphi(\infty)-\varphi(0)$	Φ
2	7.51	-6.23	-1.22	$+3.95$	3.89
4	1.88	-3.12	-1.01	$+0.82$	3.07
6	0.83	-2.08	-0.87	$+0.31$	2.42

merical equivalence of the two formulas.

We also found a proof that the two contributions must be equal. Our proof, which is given in detail in the Appendix, does not specifically rely on the density functional formalism. Instead the theorem is proved by a certain integration of a single-particle Schrödinger's equation. The explicit result we prove is that

$$\int_{-\infty}^{\infty} dx\left(-\frac{1}{n_0}\frac{dn(x)}{dx}\right)v_{\text{eff}}(x) = v_{\text{eff}}(x = -\infty) + \tfrac{2}{5}E_{\text{KE}} ,$$
(22)

where $v_{\text{eff}}(x)$ is the effective local potential acting on an electron. Lang and Kohn used a local density approximation (LDA) to the exchange correlation energy functional thereby yielding

$$v_{\text{eff}}(\vec{r}) = \varphi(\vec{r}) + E_x(n(\vec{r})) + E_c'(n(\vec{r})) ,$$
(23)

where $n(\vec{r})$ is determined self-consistently by solving Schrödinger's equation for single-particle states, Ψ_i and then summing up their density contributions:

$$n(\vec{r}) = \sum_i^{E_F} |\Psi_i(\vec{r})|^2 .$$

The crux of our proof lies in this prescription for determining $n(\vec{r})$.

One may also examine the choice of $-(1/n_0 A) \times dn(x)/dx$ for $n_a(\vec{r})$. In Fig. 1 we have plotted an "exact" $An_a(x)$, based on the approximation (23), and compared it with $-(1/n_0)\,dn(x)/dx$ computed from the density for this model. The two curves are similar but not identical. The reason we obtain the same work function as Lang and Kohn even though in the heuristic argument given above we use the approximate $-(1/n_0 A)\,dn/dx$ is because we have presumed the validity of (4) for the semi-infinite metal with only the Thomas-Fermi term used for the kinetic energy. The cancellation of these two errors is remarkable.

Another way to view the equivalence of our result with that of Lang and Kohn is to rewrite (22),

using the v_{eff} of (23) plus Eqs. (19) and (20), as

$$\varphi(0) - \varphi(-\infty) = \frac{\partial}{\partial n}(n\epsilon)\Big|_{n_0} - \epsilon\Big|_{n_0} = n_0\frac{\partial\epsilon}{\partial n}\Big|_{n_0} ,$$
(24)

where we emphasize that ϵ is given by Eq. (5) and that $n(\vec{r})$, and consequently $\varphi(\vec{r})$, is determined by using the LDA. Our proof of (24) remains valid if one were to change the density dependence of ϵ, but it breaks down if one were to use a more correct—specifically, nonlocal—treatment of the exchange correlation energy functional. However, a theorem recently proved by Budd and Vannimenus[7] gives the generalization of our formal result (24) to an exact treatment of jellium. Their result is identical to (24) except that ϵ is now the exact (and unknown) energy functional of the bulk jellium, ϵ^e, say; and $\varphi(0) - \varphi(-\infty)$ is the exact electron potential-energy difference. Budd and Vannimenus obtain their theorem by considering the energy changes which occur from an infinitesimal change in the positive background. Their theorem allows a direct generalization of the equivalence of our result with that of Lang and Kohn:

$$\Phi = [\varphi^e(\infty) - \varphi^e(-\infty)] - \frac{\partial}{\partial n}(n\epsilon^e)\Big|_{n_0}$$
(12')

$$= [\varphi^e(\infty) - \varphi^e(0)] - \epsilon^e\Big|_{n_0} .$$
(21')

Budd and Vannimenus originally proposed that the extent to which (24) is satisfied in an approximate calculation is a meaningful test of the approximation. They later withdrew this assertion, and proposed instead that the numerical test only measured the self-consistency of the Lang-Kohn computations. Our results support this latter conclusion. Their numerical test is essentially the same as that of our Table I. The theorem that we prove here demonstrates that (24) is exactly satisfied within the LDA. Hence any numerical inequality of (24) within LDA is only a measure of "computing"
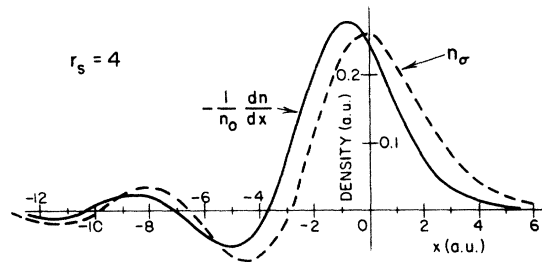

FIG. 1. Top curve compares the surface charge distribution $An_a(x)$ found by Lang and Kohn against $-n_0^{-1}dn/dx$. The two curves are similar but not identical. Both are normalized to one unit of charge obtained by integrating over all dx. Atomic units are used throughout. Numerical data supplied by Dr. N. D. Lang.

accuracy and self-consistency in obtaining $n(x)$, rather than a direct measure of physical validity. It is certainly intriguing, though, that (24) should be true both in an exact treatment and in LDA.

Finally we remark that there is an appealing physical interpretation to the new formula (21) for the work function. We may view Φ as the net energy required to take an electron off the surface to infinity [thereby doing an amount of work $\varphi(\infty) - \varphi(0)$] and also (after relaxation) to change the ground state energy of the bulk metal from $N\epsilon(x = -\infty)$ to $(N-1)\epsilon(x = -\infty)$. Combining these two energy changes we get $\Phi = [\varphi(\infty) - \varphi(0)] - \epsilon(x = -\infty)$, which is Eq. (21). The choice of $x = 0$ to represent the surface position is reasonable here since that point determines the center of mass to the electron density change:

$$\int_{-\infty}^{\infty} dx \left(-\frac{1}{n_0}\frac{dn(x)}{dx}\right)x = 0 \ .$$

This result is proved in the Appendix. By the above argument we see that the work function may be related to the ground-state energy per electron of the bulk metal. Again, this statement is true either, as shown here, within LDA or, as shown by Budd and Vannimenus, within an exact treatment of jellium.

APPENDIX: MATHEMATICAL PROOFS

The first proof is that

$$\varphi(0) = \int_{-\infty}^{\infty} dx\,\varphi(x)\left(-\frac{1}{n_0}\frac{\partial n}{\partial x}\right) , \tag{A1}$$

where

$$\varphi(x) = 4\pi e^2 \int_{-\infty}^{x} dx'(x'-x)f(x') + \varphi(-\infty) \ . \tag{A2}$$

This is proved by adding and subtracting the δ function $\delta(x)$ to the integrand

$$\int_{-\infty}^{\infty} dx\,\varphi(x)\left(\delta(x) - \frac{1}{n_0}\frac{\partial f}{\partial x}\right) . \tag{A3}$$

The first term gives $\varphi(0)$, while we must show the second term to be zero. This is done by integrating by parts to get the expression

$$-\frac{1}{n_0}\int_{-\infty}^{\infty} dx\,\varphi(x)\frac{\partial f}{\partial x} = \frac{1}{n_0}\int_{-\infty}^{\infty} dx\,f(x)\frac{\partial\varphi}{\partial x}$$

$$= -\frac{4\pi e^2}{n_0}\int_{-\infty}^{\infty} dx\,f(x)\int_{-\infty}^{x} dx'\,f(x')$$

$$= -\frac{4\pi e^2}{n_0}\int_{-\infty}^{\infty} dx'\,f(x')\int_{x'}^{\infty} dx\,f(x) , \tag{A4}$$

where the last identity results from interchanging the order of integration. If we add the last two expressions together and divide by 2, then

$$\int_{-\infty}^{\infty} dx\,\varphi(x)\left(-\frac{1}{n_0}\frac{\partial n}{\partial x}\right) = \varphi(0) - \frac{2\pi e^2}{n_0}\left(\int_{-\infty}^{\infty} dx\,f(x)\right)^2 . \tag{A5}$$

The last term is zero because of the charge neutrality of the surface

$$0 = \int_{-\infty}^{\infty} dx\,f(x) \ . \tag{A6}$$

This neutrality has been assumed by all workers in this field.

The distribution $-(1/n_0)\,\partial n/\partial x$ has an interesting property if it is interpreted as a surface charge density. The center of mass of the charge density

$$x_0 = \int_{-\infty}^{\infty} x\,dx\left(-\frac{1}{n_0}\frac{\partial n}{\partial x}\right) = 0 \tag{A7}$$

is identically zero. This is the point which effectively locates the metal surface in calculations of image charges $e^2/4|x - x_0|$ or electric field potentials $eE(x - x_0)$.[8]

The proof of (A7) is very similar to that of (A1). In the definition of x_0, one adds and subtracts a delta function from the integrand

$$x_0 = \int_{-\infty}^{\infty} x\,dx\left(\delta(x) - \frac{1}{n_0}\frac{\partial f}{\partial x}\right) . \tag{A8}$$

The first term is obviously zero, while the second term becomes zero after an integration by parts.

The last proof is for (22) which is the important theorem. In the jellium model, the eigenfunctions are plane waves parallel to the surface, and $\Psi_k(x)$ perpendicular to it

$$\Psi_{k_\perp,k}(r) = e^{i\vec{k}_\perp \cdot \vec{r}}\Psi_k(x) \ . \tag{A9}$$

We may take the $\Psi_k(x)$ as real-valued functions. The charge density is obtained by summing over all occupied electron levels

$$n(x) = \frac{2}{V}\sum_{k_\perp,k}\Psi_k(x)^2 = \frac{1}{\pi^2}\int_0^{k_F} dk\,(k_F^2 - k^2)\Psi_k(x)^2 \ . \tag{A10}$$

The wave functions $\Psi_k(x)$ are obtained as a solution to Schrödinger's equation

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + v_{\rm eff}(x) - v_{\rm eff}(-\infty) - \frac{\hbar^2 k^2}{2m}\right]\Psi_k = 0 , \tag{A11}$$

where $v_{\rm eff}(x)$ is defined in (23). This is the self-consistent procedure used by Lang and Kohn for calculating $n(x)$.[9] Our proof does not depend upon the form of $v_{\rm eff}$, except that it goes to a constant value $v_{\rm eff}(-\infty)$ in the bulk metal.

Multiply Schrödinger's equation by $2\,\partial\Psi_k/\partial x$ and obtain

$$-\frac{\hbar^2}{2m}\frac{d}{dx}\left(\frac{d}{dx}\Psi_k\right)^2 + \frac{d}{dx}(\Psi_k)^2\left[v_{\text{eff}}(x) - v_{\text{eff}}(-\infty) - \frac{\hbar^2 k^2}{2m}\right] = 0 \ . \tag{A12}$$

Integrate dx over all space and get

$$+\int_{-\infty}^{\infty} dx\, v_{\text{eff}}(x)\frac{d}{dx}(\Psi_k)^2 = \left[\left(v_{\text{eff}}(-\infty) + \frac{\hbar^2 k^2}{2m}\right)[\Psi_k(x)]^2 + \frac{\hbar^2}{2m}\left(\frac{d\Psi_k}{dx}\right)^2\right]\Bigg|_{-\infty}^{\infty} \ . \tag{A13}$$

All terms are zero in the vacuum $x = +\infty$

$$-\int_{-\infty}^{\infty} dx\, v_{\text{eff}}(x)\frac{d}{dx}(\Psi_k)^2 = \left(v_{\text{eff}}(-\infty) + \frac{\hbar^2 k^2}{2m}\right)[\Psi_k(-\infty)]^2 + \frac{\hbar^2}{2m}\left(\frac{d\Psi_k}{dx}\right)^2_{-\infty} \ . \tag{A14}$$

Summing over all occupied electron levels and dividing by n_0 yields the

$$\int_{-\infty}^{\infty} dx\, v_{\text{eff}}(x)\left(-\frac{1}{n_0}\frac{dn}{dx}\right) = v_{\text{eff}}(-\infty) + \frac{1}{n_0}\frac{2}{V}\sum_{k_{\perp},k}\frac{\hbar^2}{2m}\left[k^2\Psi_k(-\infty)^2 + \left(\frac{d\Psi_k}{dx}(-\infty)\right)^2\right] \ . \tag{A15}$$

The two kinetic-energy terms are evaluated by noting that the wave function Ψ has the form $\sin(kx + \delta)$ far from the surface, so these terms give

$$\frac{1}{n_0}\frac{2}{V}\sum_{k_{\perp},k}\hbar^2 k^2/2m = \tfrac{2}{5}E_F(n_0) \tag{A16}$$

which does yield the desired result (22). Since

$$\int_{-\infty}^{\infty} dx\, E_F(n(x))\left(-\frac{1}{n_0}\frac{dn}{dx}\right) = \tfrac{3}{5}E_F(n_0) \ , \tag{A17}$$

this can also be written in the form

$$\int dx\left(-\frac{1}{n_0}\frac{dn}{dx}\right)[v_{\text{eff}}(x) + E_F(n(x))] = E_F(n_0) + v_{\text{eff}}(-\infty) \tag{A18}$$

which summarizes the equivalence of the Lang-Kohn result on the right and our results on the left.

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