Self-Consistent Many-Electron Theory of Electron Work Functions and Surface Potential Characteristics for Selected Metals*

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Electron work functions, surface potentials, and electron number density distributions and electric fields in the surface region of 26 metals are calculated from first principles within the free-electron model. The number of free electrons per atom is taken as the group number as listed in the Periodic Table. Grain orientation effects are not considered. The calculation proceeds from an expression of the total energy as a functional of the electron number density including exchange and correlation energies as well as a first inhomogeneity term. The self-consistent solution is then obtained via a variational procedure akin to the Ritz method. Surface barriers are found, in most cases, to be due principally to many-body effects, but dipole barriers are small *only* for a number of alkali metals, becoming quite large for the transition metals. As one might expect, surface energies are found to be inadequately described by this model which neglects atomistic effects. Considering the simplicity of the model, reasonable results are obtained for electron work functions and surface potential characteristics for all metals studied, maximum electron densities varying by a factor of over 60.

I. INTRODUCTION

THE wealth of experimental data available today on electronic work functions of bare metal surfaces[1] is not at all matched by theoretical calculations. There have been numerous empirical correlations made relating the electron work function of metals to atomic volume, compressibility, the first atomic ionization potential, the energy of the lattice, surface energy, and electronegativity. These efforts are enumerated by Samsonov *et al.*[2] (see also Dobretsov and Matskevich[3] and Steiner and Gyftopoulos[4]). Also, some efforts have been made toward formulating a first-principles description of various aspects of this quantity[5–9] for certain metals. However, such calculations of the total (bulk plus surface contribution) electron work function have been provided only for the alkali metals. The most sophisticated of these is that formulated by Bardeen[10] for Na. A free-electron model was used and the Hartree-Fock equations were solved approximately.

This is in contrast to the progress made in overlapping areas. For example, many-electron[11] and atomistic effects[12] have been included in theoretical studies of bulk metallic properties of *many* metals. Likewise, many-electron effects and some atomistic effects have been included in the theory of adsorption on metals[13] using modern formulations of the many-electron problem.

A second topic considered here which is related to the electron work function is that of the surface potential. Recently, a calculation of the surface potential of Na which refines Bardeen's work by making use of a modern many-electron formulation[11] has been provided by Loucks and Cutler[14] (see also Ref. 15). However, these authors neglect the effect of the surface dipole potential and place an infinitely high potential barrier at the surface in order to calculate wave functions. The first assumption may well be reasonable for Na, but it will be shown that dipole barriers cannot be neglected for most of the metals studied here. The second assumption, of course, rules out self-consistency. More recently, Bennett and Duke[16,17] have introduced self-consistency into a many-electron calculation of the one-electron potential at a bimetallic interface.

A small step is made here toward bringing bare surface work function theory up to the level of sophistication of neighboring fields, and in the process to gain a greater knowledge about metal surface properties in general. A calculation of the work function is presented here for 26 metals including Na, using the jellium model. In addition, the electrostatic (double-layer) barrier, representative electric fields, electron number density distributions, and one-electron potentials were calculated for the surface region. The jellium or free-electron

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[1] V. S. Fomenko, *Handbook of Thermionic Properties* (Plenum Press, Inc., New York, 1966).
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[3] L. N. Dobretsov and T. L. Matskevich, Zh. Tekhn. Fiz. **36**, 1449 (1966) [English transl.: Soviet Phys.—Tech. Phys. **11**, 1081 (1967)].
[4] D. Steiner and E. Gyftopoulos, in Report on the Physical Electronics Conference, MIT, Cambridge, Mass., 1967, p. 160 (unpublished).
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[6] W. Oldekop and F. Sauter, Z. Physik **136**, 534 (1954).
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[8] M. Kaplit, in *Thermionic Conversion Specialist Conference* (Institute of Electrical and Electronic Engineers, New York, 1966), p. 387.
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[11] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), pp. 60–61.
[12] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).
[13] J. W. Gadzuk, Solid State Commun. **5**, 743 (1967).
[14] T. L. Loucks and P. H. Cutler, J. Phys. Chem. Solids **25**, 105 (1964).
[15] R. W. Davies, Surface Sci. **11**, 419 (1968).
[16] A. J. Bennett and C. B. Duke, Phys. Rev. **160**, 541 (1967).
[17] A. J. Bennett and C. B. Duke, in Abstracts of the Fourth International Materials Symposium, Lawrence Radiation Laboratory, 1968 (unpublished).

model is used here so that many surface parameters can be calculated rather simply. Conclusions can then be made as to which surface characteristics are adequately described in this model and which require further sophistication in their description. Also, our understanding of the metal surface can be considerably enhanced without undue effort. A recent formulation[18] of the inhomogeneous electron gas which includes Coulomb correlations was used in an approximate self-consistent first-principles solution of the model. The number of free electrons per atom was taken as the group number as listed in the Periodic Table. Grain orientation effects were not considered.

We found that exchange and correlation potentials make up the major part of the surface barrier for most of the metals considered. However, the ordinary Coulomb potential barriers are significant for all of these metals except Cs, Rb, K, and Na. Also, the results obtained using the simple model described previously show encouraging agreement with available experimental data for all the metals considered.

This paper is divided into four major sections. In Sec. II the basic equations used are derived. Section III is devoted to a comparison of some of the results obtained with existing theoretical findings. Results for 26 metals and comparison with experimental data are presented in Sec. IV. Concluding remarks are given in Sec. V.

II. DERIVATIONS

Following Bardeen, the free-electron or "jellium"[5,17,19–23] model with planar surface (see Fig. 1) is used. Bardeen's use of the Hartree-Fock equations is not followed, however, because it provided much numerical difficulty. Also, since the Hartree-Fock equations neglect antiparallel spin correlations, attempts to take such correlations into account are necessarily *ad hoc* in nature.[24] Hohenberg and Kohn[18] (see also Refs. 25–27) have recently derived a powerful formulation of the many-electron problem. This scheme, which uses the electron number density as the basic variable, provides considerable simplification and includes all many-electron effects in the original formulation. Thus it will be used here.

Hohenberg and Kohn[18] (HK) have shown that the ground-state energy E_v of a confined interacting in-

[18] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[19] C. Herring, *Metal Interfaces* (American Society for Metals, Metals Park, Ohio, 1952), p. 16.
[20] H. J. Juretschke, in *The Surface Chemistry of Metals and Semiconductors*, edited by H. Gatos (John Wiley & Sons, Inc., New York, 1960), p. 46.
[21] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).
[22] C. H. Kelley, Ph.D. thesis, Polytechnical Institute of Brooklyn, 1954 (unpublished).
[23] J. W. Gadzuk, Surface Sci. **6**, 133 (1967).
[24] J. Bardeen, Surface Sci. **2**, 385 (1964).
[25] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[26] B. Y. Tong and L. J. Sham, Phys. Rev. **144**, 1 (1966).
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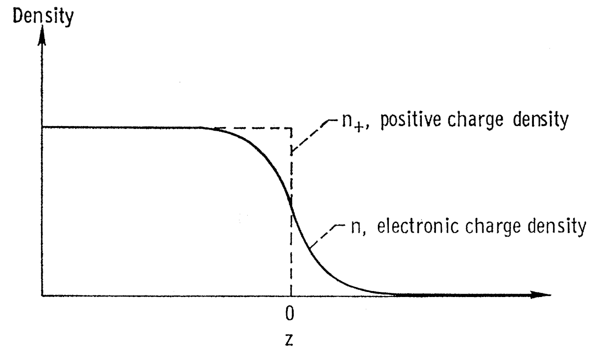

FIG. 1. Electronic and positive charge densities for the jellium model.

homogeneous electron gas can be written as a functional of the electron number density $n(\mathbf{r})$. Further, they have shown that $E_v[n]$ assumes a minimum value for the correct $n(\mathbf{r})$, if admissible density functions conserve the total number of electrons. Thus, $n(\mathbf{r})$ can be determined from

$$(\delta/\delta n)\{E_v[n]-\mu N\}=0\,, \tag{2.1}$$

where μ is a Lagrange multiplier such that[28] $\mu=\partial E_v/\partial N$, and $N=\int n(\mathbf{r})d\mathbf{r}$. HK write[29]

$$E_v[n]=\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} +\frac{1}{2}\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'+G[n]\,, \tag{2.2a}$$

where $v(\mathbf{r})$ is a static external potential, $G[n]\equiv T_s[n]+E_{xc}[n]$, $T_s[n]$ is the kinetic energy of a system of noninteracting electrons with the same density $n(\mathbf{r})$, and $E_{xc}[n]$ is then the exchange and correlation energy of an interacting system.

HK derive an expansion of $G[n]$ originally for the case of slowly varying n in successive orders of the gradient operator ∇ acting on $n(\mathbf{r})$ which can be written[30]

$$G[n]=\tfrac{3}{10}(3\pi^2)^{2/3}\int n^{5/3}d\mathbf{r}-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int n^{4/3}d\mathbf{r} -0.056\int\frac{n^{4/3}}{0.079+n^{1/3}}d\mathbf{r}+\frac{1}{72}\int\frac{(\nabla n)^2}{n}d\mathbf{r}+\cdots. \tag{2.2b}$$

The integrands of the first three terms on the right-hand side of Eq. (2.2b) represent, respectively, the kinetic, exchange, and correlation energy densities of a uniform electron gas of density n. The Wigner interpolation formula was used to represent the correlation energy of a homogeneous electron gas at metallic densi-

[28] L. Hulthén, Physik **95**, 789 (1935).
[29] Atomic units are used throughout this paper, except where noted otherwise.
[30] Equations (87) and (89) of Ref. 16, converting from Ry to a.u. in the former equation.

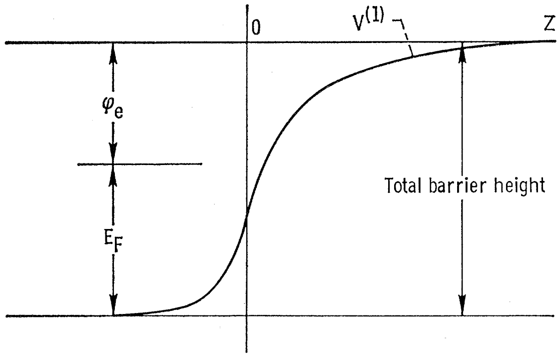

FIG. 2. Relation between the electron work function φ_e, the Fermi energy E_F, and the effective one-electron potential energy for a state at the top of the Fermi distributions $V^{(1)}$.

ties. The fourth term is the first of the inhomogeneity terms, i.e., those terms containing one or higher orders of the gradient operator acting on n.

Several comments about Eq. (2.2b) are in order. First, it is shown elsewhere[31] that at least some inhomogeneity terms must be included in a work function calculation. It is well known that a simple Thomas-Fermi theory predicts that the work function of any physical system is zero. We have shown[31] that including the homogeneous electron gas exchange and correlation energy terms, but not including inhomogeneity terms, leads to a predicted work function which is nonzero but is the same for essentially any system. It will be seen in the following that the addition of the first inhomogeneity term alleviates this anomaly.

Secondly, the random-phase approximation (RPA) was used by HK to derive the factor $1/72n$ in the first inhomogeneity term. Although the RPA has exhibited failings at electron densities as low as those found in conduction bands,[11] this inhomogeneity correction to the total energy apparently has a rather wide range of applicability as shown by the successes of Kirzhnits[32] and of Kalitkin.[33] Kirzhnits considered isolated noble-gas atoms and Kalitkin compared his results with experimental bulk properties of solids. Also, the RPA has been used with some success in metal surface theory.[13,34,15] Thus it is used here.

Third, HK note that a "gradient" expansion of which the sum of the integrands in Eq. (2.2b) is an example does *not converge*[35] for actual electronic systems due to number variations with position. However, they expect it to be useful in the sense of asymptotic convergence[36] for sufficiently slowly varying number densities. A formulation based on the "gradient" expansion has exhibited some successes even for the case of atoms[26] where the density variation is rather rapid. Also, Kirzhnits[32] investigated explicitly the convergence of an expansion of $E_v[n]$ in successive powers of $\hbar$ not including correlation energies. He calculated $E_v[n]$ for the argon atom, and found in an approximate manner "excellent convergence of the approximation process," at least when his first four inhomogeneity terms were included. Finally, HK note that quantum density oscillations are not included in the expansion given in Eq. (2.2b). However, it has been reported[17] for a jellium model with planar surface that the Friedel oscillations occurring inside the metal are greatly diminished by requiring that the surface potential be self-consistent with the electron number density distribution. Since a self-consistent calculation is done here, they are neglected. Finally, corrections to the Thomas-Fermi equation derived by expansion procedures have been shown by Schey *et al.*[37] to be pejorative in many instances. However, they note that expansions of the total energy (as we use here) lead to "remarkable improvement."

Keeping only the first inhomogeneity term and combining Eqs. (2.1) and (2.2), one obtains for our model

$$\frac{d^2n}{dZ^2}-\frac{1}{2n}\left(\frac{dn}{dZ}\right)^2=36\Bigg[\tfrac{1}{2}(3\pi^2)^{2/3}n^{5/3}+(\varphi-\mu)n-\left(\frac{3}{\pi}\right)^{1/3}n^{4/3}-\frac{0.056n^{5/3}+0.0059n^{4/3}}{(0.079+n^{1/3})^2}\Bigg], \quad (2.3)$$

where, for self-consistency, $d^2\varphi/dZ^2=4\pi[n_+H(-Z)-n]$, n_+ is the positive jellium charge density, $H(Z)$ is the Heaviside (step) function, Z is the Cartesian coordinate taken on an axis normal to the surface, with $Z=0$ at the jellium surface,

$$\varphi\equiv v(\mathbf{r})+\int\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}',$$

and, in this case, $v(\mathbf{r})$ is the negative of the potential of the ion distribution.

Note that in the jellium model, $n\to n_+$ and all derivatives of $n\to 0$ as $Z\to-\infty$. Also, $\varphi_e=$ electron work function[10] $\equiv-(\partial E_v/\partial N)_{N=N_+}=-\mu$. Thus one obtains ($\varphi_e$ is described in Fig. 2)

$$\varphi_e=-\varphi(-\infty)-\tfrac{1}{2}(3\pi^2)^{2/3}n_+^{2/3}+\frac{0.056n_+^{2/3}+0.0059n_+^{1/3}}{(0.079+n_+^{1/3})^2}+\left(\frac{3}{\pi}\right)^{1/3}n_+^{1/3}, \quad (2.4)$$

where $\varphi(-\infty)$ represents the value φ asymptotically approaches deep within the metal and φ is set equal to zero at large distances from the metal.

It should be remembered that this is a many-electron calculation. However, Kohn and Sham[25] have shown

[31] J. R. Smith (to be published); also see Ph.D. thesis.
[32] D. A. Kirzhnits, Zh. Eksperim. i Teor. Fiz. **32**, 115 (1957) [English transl.: Soviet Phys.—JETP **5**, 64 (1957)].
[33] N. N. Kalitkin, Zh. Eksperim. i Teor. Fiz. **38**, 1534 (1960) [English transl.: Soviet Phys.—JETP **11**, 1106 (1960)].
[34] P. A. Fedders, Phys. Rev. **153**, 438 (1967).
[35] S. Ma and K. A. Brueckner, Phys. Rev. **165**, 18 (1968).
[36] P. Morse and H. Feshbach, *Methods of Theoretical Physic* (McGraw-Hill Book Co., New York, 1953), Vol. I, p. 434.
[37] H. Schey *et al.*, Phys. Rev. **137**, A709 (1965).

that it is possible, formally, to replace the equations of the many-electron problem by an equivalent set of one-electron equations. The effective one-electron potential energy $V^{(1)}$ is given formally by

$$V^{(1)}=\frac{\delta E_{xc}[n]}{\delta n}+\varphi. \tag{2.5}$$

A comparison of Kirzhnits's[32] first inhomogeneity term in his expansion in powers of $\hbar$ of the Hartree total energy and that in Eq. (2.2b) shows that they are identical. Thus, the first inhomogeneity term contributes only to $T_s[n]$ in the RPA. So, to $O(|\nabla n|^2)$ in E_v,

$$V^{(1)}=\varphi-\left(\frac{3}{\pi}\right)^{1/3}n^{1/3}-\frac{0.056n^{2/3}+0.0059n^{1/3}}{(0.079+n^{1/3})^2}. \tag{2.6}$$

$V^{(1)}$ as given in Eq. (2.6) is just the potential energy that one would obtain[25] for the highest one-electron energy state of a uniform electron gas of density n in its ground state. Thus it follows that, at least to $O(|\nabla n|^2)$ in E_v, $V^{(1)}$ is equivalent to the effective potential energy for a state at the top of local Fermi distributions.

$V^{(1)}$ can be obtained immediately through Eq. (2.6) once the many-electron problem is solved, and it is exhibited in several of the figures for the reader who is interested in a one-electron calculation.

In order to obtain n, it is certainly simpler to solve Eq. (2.3) than, e.g., a set of Hartree-Fock equations. However, we will simplify the solution of Eq. (2.1) still further. Let us assume that the extremal of Eq. (2.1) belongs, to a good approximation, to the following family of functions[8,21,38]:

$$\begin{aligned} n&=n_+-\tfrac{1}{2}n_+e^{\beta Z}, \quad Z<0\\ n&=\tfrac{1}{2}n_+e^{-\beta Z}, \quad Z>0 \end{aligned} \tag{2.7}$$

where β is a family parameter.

Note that for every value of β the family (2.7) satisfies certain requirements of self-consistency. First, n asymptotically approaches n_+ in the metal interior and zero in the vacuum region outside the metal. Secondly,

$$\int_{-\infty}^{+\infty}[n-n_+H(-Z)]dZ=0.$$

There are no experimental data on n which provide a direct test of the validity of the family (2.7). It will be shown below, however, that the results obtained using these simple functions are in at least as good an agreement with experiment as could be expected using a flat-surfaced jellium model.

The corresponding Coulomb potential is

$$\begin{aligned} \varphi&=2\pi n_+e^{\beta Z}/\beta^2-4\pi n_+/\beta^2, \quad Z<0\\ \varphi&=-2\pi n_+e^{-\beta Z}/\beta^2, \quad Z>0. \end{aligned} \tag{2.8}$$

[38] T. Toya, J. Res. Inst. Catalysis Hokkaido Univ. 8, 209 (1961).

Equation (2.1) becomes

$$dE_v[n]/d\beta=0$$

or, equivalently,

$$d\sigma/d\beta=0, \tag{2.9}$$

where

$$\sigma=\int_{-\infty}^{\infty}dZ\{\epsilon_v[n]-\epsilon_v[n_+H(-Z)]\}, \tag{2.10}$$

in which $\epsilon_v[n]$ is the energy density, i.e., $E_v[n]=\int\epsilon_v[n]d\mathbf{r}$; and σ is the surface energy, or the energy necessary to cleave a metal per unit area of new surface formed. Thus σ is the total energy of the separate pieces after splitting minus the total energy of the unsplit block.

A simple result of analytical manipulations of the terms on the right-hand side of Eq. (2.10) up to and including the first inhomogeneity term is provided below, except for the correlation energy integral over the range $-\infty\leq Z\leq 0$. This last term was easily programmed, and is designated below[39] as $I(n_+)/\beta$.

This gives[40]

$$\begin{aligned}\sigma=\frac{\pi n_+^2}{2\beta^3}-\tfrac{3}{10}(3\pi^2)^{2/3}\frac{n_+^{5/3}}{\beta}(0.572)\\ +\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\frac{n_+^{4/3}}{\beta}(0.339)+\frac{I(n_+)}{\beta}-\frac{0.084n_+}{\beta}\\ \times\left(a^2-\tfrac{1}{2}a+\tfrac{1}{3}+a^3\ln\frac{a}{a+1}\right)+\frac{\beta n_+}{72}\ln 2,\end{aligned} \tag{2.11}$$

where terms are given in the same order as those in Eq. (2.2), and where $a=2^{1/3}\times 0.079/n_+^{1/3}$.

Thus β can be determined by combining Eqs. (2.11) and (2.9), and this result can be used to determine n and φ via Eqs. (2.7) and (2.8). With these, the quantities φ_e and $V^{(1)}$ can be determined immediately from Eqs. (2.4) and (2.6), respectively.

III. COMPARISON OF RESULTS WITH THOSE OF OTHER CALCULATIONS

Work Function of Na

Results obtained here, as well as Bardeen's results, are listed in Table I. Wigner's uncorrected[10] interpolation formula was used in this instance, so that a more direct comparison could be made with Bardeen's work.

Considering the different approximations made in the two calculations, the agreement is quite good. Notice that the work function and Coulomb barrier are 0.39 V higher than Bardeen's results. No decision can be made based on the experimental data as to which theoretical

[39] A table of values of $I(n_+)$ for all metals is available and will be sent upon request.

[40] Note that the result given earlier (Ref. 21) for the first term is slightly incorrect.

TABLE I. Comparison with Bardeen's results for work function, Coulomb barrier, and surface energy for Na.

	Double-layer moment (eV)		Work function (eV)			Surface energy (J/m^2)	
	Here	Bardeen	Here[a]	Bardeen	Experimental[b]	Here	Bardeen[c]
Neglecting correlation energies	0.786	0.4	2.74	2.35	2.35	0.112	0.088
	0.978	$\sim$1					
Neglecting exchange and correlation energies	3.12	$\sim$4					

[a] Wigner's uncorrected interpolation formula (Ref. 10) was used here because Bardeen used it.
[b] Value listed for work function is Fomenko's recommended value (Ref. 1).
[c] The actual calculation of the surface energy using Bardeen's results was done by Huntington (Ref. 41).

value is more accurate. This is because, first, the value listed is for polycrystalline Na, and, second, there are inaccuracies even in the knowledge of this value. If our results turn out to be more accurate, then the difference may be explained by the fact that, as stated by Loucks,[14] only a partially self-consistent solution was achieved by Bardeen with respect to the electrostatic part of the problem, since the exchange potentials were chosen at the beginning and held fixed throughout. But, as noted earlier, it has been reported[17] that the Friedel oscillations inside the metal are greatly diminished by self-consistency requirements. Since these oscillations lead to a "humping up" of electronic charge inside the metal which lowers the dipole moment and work function, their overemphasis could lead to values of these quantities which are too low.

Finally, it is clear that this calculation supports Bardeen's conclusion that the surface barrier of Na is due primarily to exchange and polarization forces with ordinary electrostatic forces playing a minor role.

Surface Energy

The surface energy for Na was calculated by Huntington,[41] using Bardeen's potential.[10] Table I shows that

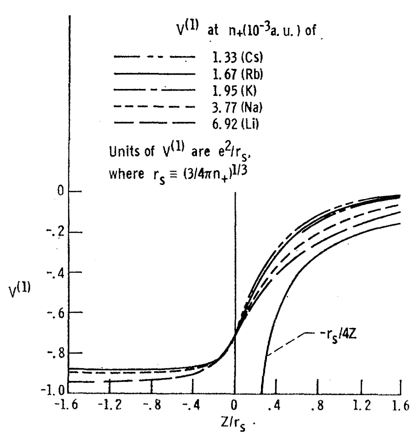

FIG. 3. $V^{(1)}$ in the surface region of the alkali metals.

[41] H. B. Huntington, Phys. Rev. 81, 1035 (1951).

the surface energy of Na calculated here agrees rather well with that calculated by Huntington. Neither is in good agreement with the experimental value[20] of 0.240 J/m^2. Herring,[19] however, has pointed out that it is not "fair" to compare the surface energy σ of a jellium metal with an actual metal of the same electron density. Table II shows values of σ for Na, Li, and K. The disagreement with experiment is even more pronounced for Li than for Na and, in fact, σ goes negative for $n_+ \geq 13\times10^{-3}$. Thus further results were not listed.

It should be noted that the electron work functions and surface potential characteristics depend on the variation of σ [e.g., $d\sigma/d\beta$ in Eq. (2.9)] and not on the value of σ itself. Thus, the fact that the surface energy results do not agree with experiment does not imply that the results for the work functions and surface potentials should not be trusted.

Na Surface Potential Characteristics

To compare our $V^{(1)}$ for Na (see Figs. 3 and 4) with the results of Loucks and Cutler[14] (see their Fig. 5), one will have to bear in mind that our potential pertains to an electron at the top of the Fermi distributions, whereas they averaged their exchange contribution. Also, as mentioned earlier, they neglect the small Coulomb contribution. Their potential curves are qualitatively similar to $V^{(1)}$, except that their curves exhibit noticeable damped oscillatory behavior in the interior of the metal. As previously noted, Bennett *et al.*[17] have concluded that these oscillations are exaggerated by lack of self-consistency. Figures 3 and 4 present curves of $V^{(1)}$ and relative electron number densities, respectively, in the surface region of the alkali metals as a function of Z/r_s, where $r_s \equiv (3/4\pi n_+)^{1/3}$.

TABLE II. Surface energies of K, Li, and Na—comparison of results.

Metal	Surface energy (J/m^2) Theory	Experimental[a]
K	0.0688	0.146
Na	0.111	0.240
Li	0.132	0.510

[a] Reference 20.

IV. RESULTS FOR SELECTED METALS

Method of Selection

It seems reasonable that all metals usually regarded[11] as "free-electron-like" in their bulk properties could be treated within this model. In addition, the surface properties of even the *transition* metals have been described with a certain degree of success within the free-electron model. Examples of such successful applications are the Richardson-Dushman equation describing thermionic emission, the Fowler-Nordheim vacuum field electron emission theory,[42] the plasma oscillation characteristic loss theory,[43] and the analysis of periodic deviations in the thermionic Schottky effect.[44] Thus, those metals which were in some way amenable to analysis using the free-electron model were chosen for consideration and are listed in Tables III and IV.

The characteristics of the metals enter into the model only through the quantity n_+. Thus values of n_a, the number of conduction electrons per atom, must be designated. For all but the simplest metals this choice is not obvious.[4,45–47] However, some properties such as Fermi energies of many simple metals[48] are well represented on a free-electron model using the group number (as listed in the Periodic Table) for n_a. The group number will be used for n_a for all metals considered here. It will be seen that this convention yields surface-barrier heights which are consistent with experiment.

TABLE III. Work functions of selected metals—comparison of results.

Metal	n_a	n_+ (10^{-3} a.u.)	β	Work function (eV) Theory	Work function (eV) Experimental[a]
Cs	1	1.33	1.33	2.64	1.81
Rb	1	1.67	1.32	2.71	2.16
K	1	1.95	1.32	2.76	2.22
Na	1	3.77	1.27	2.93	2.35
Li	1	6.92	1.24	3.11	2.38
Ag	1	8.73	1.23	3.19	4.3
Au	1	8.80	1.23	3.19	4.3
Cu	1	12.6	1.23	3.32	4.4
Ca	2	6.90	1.24	3.11	2.80
Mg	2	12.8	1.22	3.33	3.64
Cd	2	13.8	1.22	3.36	4.1
Zn	2	19.5	1.22	3.50	4.24
Be	2	35.8	1.26	3.75	3.92
La	3	12.0	1.22	3.30	3.3
Tl	3	15.4	1.22	3.40	3.7
In	3	17.0	1.22	3.44	3.8
Ga	3	22.3	1.23	3.56	3.96
Al	3	26.9	1.24	3.64	4.25
Sn	4	17.4	1.22	3.45	4.38
Pb	4	19.4	1.22	3.50	4.0
Ta	5	41.3	1.27	3.80	4.12
Nb	5	41.6	1.27	3.81	3.99
W	6	56.2	1.30	3.91	4.5
Mo	6	57.4	1.30	3.92	4.3
Re	7	70.4	1.32	3.98	5.0
Ir	8	84.2	1.34	4.02	5.3

[a] Value listed is Fomenko's recommended value (Ref. 1).

TABLE IV. Surface potential characteristics of selected metals.[a]

Metal	Electric field[b] (V/m)	Barrier height (eV) Theory[c]	Barrier height (eV) Experimental	Double layer (eV)
Cs	6.03×10^{7}	4.22		0.258
Rb	7.72×10^{7}	4.54		0.327
K	9.22×10^{7}	4.79	4.12[d]	0.386
Na	2.09×10^{8}	6.04	4.85[d]	0.794
Li	4.44×10^{8}	7.84	6.08[d]	1.55
Ag	5.62×10^{8}	8.70		1.99
Au	5.88×10^{8}	8.74		2.01
Cu	8.62×10^{8}	10.4	11.4[d]	2.91
Ca	4.42×10^{8}	7.82	5.9[d]	1.55
Mg	8.80×10^{8}	10.5	9.84[d]	2.95
Cd	9.48×10^{8}	10.8		3.18
Zn	1.31×10^{9}	12.9	15.24[d]	4.45
Be	2.12×10^{9}	17.9	17.72[d]	7.76
La	8.22×10^{8}	10.1		2.77
Tl	1.05×10^{9}	11.5		3.55
In	1.16×10^{9}	12.0		3.90
Ga	1.47×10^{9}	13.9		5.06
Al	1.71×10^{9}	15.3	16.05[d]	6.00
Sn	1.18×10^{9}	12.2		3.98
Pb	1.31×10^{9}	12.9	13.78[e]	4.43
Ta	2.34×10^{9}	19.4		8.78
Nb	2.36×10^{9}	19.5		8.84
W	2.86×10^{9}	23.0		11.4
Mo	2.89×10^{9}	23.3	22–24[f]	11.6
Re	3.25×10^{9}	26.2	27–29[f]	13.8
Ir	3.60×10^{9}	29.0		15.9

[a] The quantities listed here are obtained self-consistently with those listed in Table III.
[b] Evaluated at $Z=3a_0$.
[c] Maximum magnitude of $V^{(1)}$.
[d] Obtained by adding Fomenko's (Ref. 1) recommended work function to x-ray emission bandwidths as listed in Wilson (Ref. 48).
[e] Fermi energy as given by J. R. Anderson and A. V. Gold [Phys. Rev. 139, A1459 (1965)] is added to Fomenko's (Ref. 1) recommended work function.
[f] Reference 44.

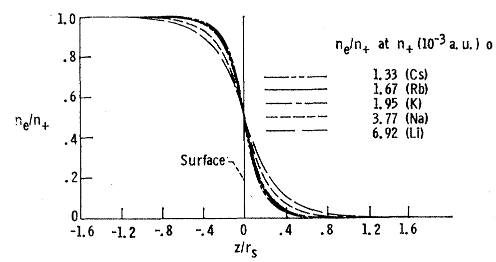

FIG. 4. Relative electron number density distribution in the surface region for the alkali metals.

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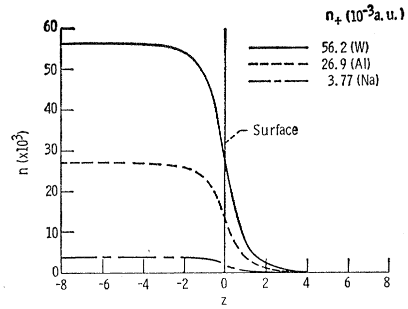

FIG. 5. Electron number density distributions in surface region for W, Al, and Cs.

For purposes of discussion, the metals are grouped according to common properties. The alkali metals, the refractory transition metals, and the noble metals are obvious groupings. The rest of the metals can easily be grouped according to group number.

As is seen from Figs. 5 and 6, the metals considered cover a wide range of electron densities, thus providing a stern test of model and method.

Electron Work Functions

Table III compares our results with the experimental values for polycrystalline metals recommended by Fomenko.[1] It should be noted that there is considerable scatter in the data that he collected.

Several comments are in order concerning the findings listed in Table III. First, the theoretical values of φ_e listed increase with increasing n_+. Second, the ordering within groups by experimental work function (e.g., low to high) is generally the same as the analogous ordering by theoretical work function. Also, the ordering of groups by average experimental and theoretical work functions, respectively, yields identical results, with the exception of the noble metals. Finally, it is seen that theoretical work functions of the low n_+ metals (principally the alkali metals) are higher than the experimental work functions. But for the rest of the metals, the theoretical value slips below the experimental value, with the difference showing some tendency to increase with n_+, again with the exception of the noble metals.

One might be tempted to ascribe the exceptions found in the case of the noble metals to the choice of $n_a=1$. That is, although this choice might be useful for calculation of certain bulk properties, it may be argued that their surface band structure[49] can be significantly different[44,50] from that of the bulk. However, a recent *surface* experimental determination of the inner potential of Cu gives a value[51] which is consistent with the use of $n_a=1$. Inclusion of grain orientation effects may clarify matters.

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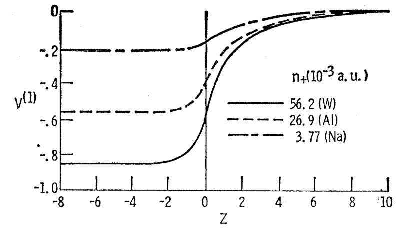

FIG. 6. $V^{(1)}$ in the surface region for W, Al, and Cs.

A decision based on comparison of experimental data and theory should be made as to the accuracy of the jellium model in the prediction of electron work functions. This decision is complicated by the fact that there are, of course, errors in the experimental data and that grain orientation effects are not included in the calculation. From the preceding discussion we have seen that there is a general agreement in the ordering of the theoretical and experimental work functions within groups and in the ordering of group average work functions. Further, the deviation of the theoretical work functions above or below the experimental values listed is within the range of variation conceivably caused by grain orientation effects for the bulk of the metals considered. But the entire range of experimental work functions is only about 2.5 V. Thus, although the theoretical values generally pass the test of comparison with experiment, it is not as stringent a test as one might desire.

But the surface potential characteristics can be turned to for further testing. It will be seen in the next section that experimental barrier heights vary by about 25 V. This should provide a much more difficult test for the theory.

Surface Potential Characteristics

The results for electric field, barrier height, and electrical double layer are listed in Table IV. Sample plots of $V^{(1)}$ are given in Figs. 3 and 6–8. Included also on some of the plots is the function $-(4Z)^{-1}$. Although all surface potentials must asymptotically approach the image potential at large distances from the metal, an

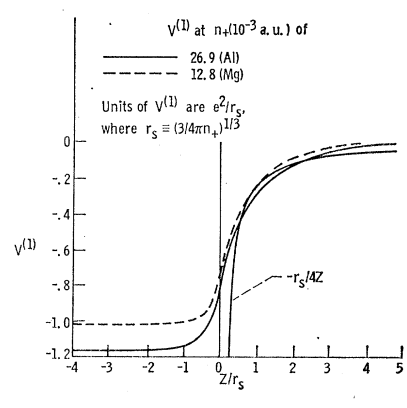

FIG. 7. $V^{(1)}$ in the surface region of Al and Mg.

ambiguity arises because it is not clear where to place the $Z=0$ plane [appropriate to the function $-(4Z)^{-1}$] with respect to the jellium surface. Thus the function $-(4Z)^{-1}$ is not necessarily the image potential, but can be used for scaling purposes.

Several trends can be inferred from the results. First, the listed barrier heights (maximum value of $V^{(1)}$) increase with increasing n_+. Second, although generally the better part of the surface barriers are due to many-body effects, the ordinary electrostatic contribution to the barrier is small *only* for the alkali metals through Na. In fact, for some of the refractory transition metals, the dipole barrier is more than half of the total barrier.

A comparison of calculated total barrier heights with experiment for electrons at the Fermi level provides another check on the validity of using the group number for n_a. Since the barrier height is quite sensitive to n_a, and since it was only desired to check reasonableness in the choice of n_a, listing of experimental values was not made exhaustive or necessarily "latest-word." In comparing our theoretical values of barrier heights with experiment, one must remember that the effective potential seen by an electron depends on its velocity. As previously pointed out, $V^{(1)}$ applies to electrons at the Fermi level and thus values of the surface barrier obtained from, say, electron interference microscopy, may well not be descriptive of the maximum magnitude of $V^{(1)}$. Also, as mentioned earlier, it is not necessarily true that the experimental barrier height should be given by the experimental value of the work function added to the experimental or theoretical bulk Fermi energy. For example, D'Haenens and Coomes[44] point out that, following this procedure, one would obtain lower total barriers than their (surface) experimental values indicate (see, however, Ref. 52). These authors explain that the energy-level system could understandably undergo modification at the surface.[20] Thus wherever (surface) experimental values of the surface barrier for electrons near the Fermi level were known to differ significantly from the sum of the bulk Fermi energy and electron work function, the result of the surface experiment was used in Table IV. A comparison of theoretical and experimental barrier heights listed in Table IV shows that the values generally agree within experimental error. This lends support to the use of the group number for n_a.

In addition, a comparison of plasma oscillation theory results with the data obtained in *surface* characteristic loss experiments can be used to determine n_a (see, e.g., Ref. 43 or Ref. 53). The results of these authors support the use of the group number for n_a for many metals.

Finally, electric fields were calculated. It follows from Eq. (2.8) and the values of β listed in Table II that the electric field $d\varphi/dZ$ varies rapidly with position, always pointing out of the metal. Now in a real metal there are very strong fields in the ion cores (experienced generally by the core and not the conduction electrons) which are not present in the jellium model. Therefore, the electric field is calculated at a somewhat arbitrary point outside the metal surface [$Z=3(a_0)$] where the result should be free of strong core field effects.

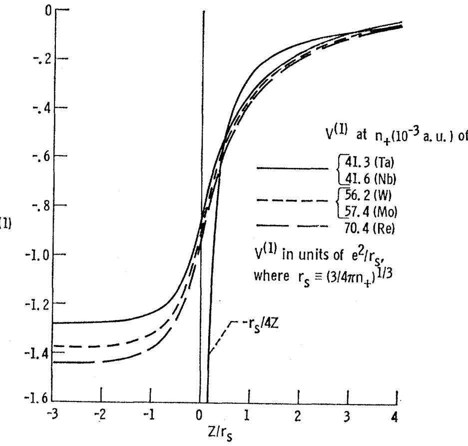

FIG. 8. $V^{(1)}$ in the surface region for selected refractory metals.

The listed values of the fields calculated at the aforementioned point increase with n_+, increasing by roughly a factor of 50 in going from the alkali metals to the refractory transition metals.

Semiempirical calculations of electric fields as seen by adsorbed particles on molybdenum[54] and tungsten[55,56] agree rather well with the theoretical values obtained here.

V. CONCLUDING REMARKS

The following generalizations can be inferred from the results obtained here:

(a) There is approximate agreement between the experimental data and the work functions and surface potential characteristics obtained here using the free-electron model. This lends support to the premise that it may be possible to calculate rather accurate values for some metal surface characteristics via introduction of refinements to this simple model. This may even be so for some of those metals whose bulk characteristics are not so easily described, e.g., the refractory transition metals.

(b) Many-body effects were found to be of importance in all cases and *ordinary electrostatic effects* are quite strong for many of the metals considered.

ACKNOWLEDGMENT

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