Surface Energy of Simple Metals: Self-Consistent Inclusion of the Ion Potential

J. P. Perdew*
Department of Physics, Rutgers University, New Brunswick, New Jersey 08903

and

R. Monnier†
NORDITA, Blegdamsvej 17, DK-2100 Copenhagen, Denmark

(Received 27 July 1976)

The surface energy for several simple metals is calculated self-consistently with use of a single variational parameter whose optimal value depends on the crystal structure and the surface plane considered. The calculation clearly demonstrates the strong dependence of the electron-density profile at the metal-vacuum interface on the discreteness of the ionic density. The method is as simple numerically as the usual jellium calculations and can probably be applied readily to more complex surface problems.

We calculate the surface energies of several simple metals and show that the perturbing effect of the ions must and can effectively be included from the outset in the self-consistent determination of the electron-density profile at the metal-vacuum interface. A knowledge of this profile is important for a quantitative understanding of all surface-related properties of simple metals (e.g., surface energy,[1] work function,[2] chemisorption,[3] and positron annihilation in metal vacancies[4]). While there exist full solutions[5] of the three-dimensional (3D) Schrödinger equation for isolated metals and certain crystal faces, we consider here approximate 1D treatments. These, to their advantage, are simple enough to show trends for large classes of metals and crystal faces and can be easily generalized to more complex surface problems. However, in existing calculations of this type, the lattice of ions is replaced by a uniform background of positive charge, and it is for this jellium model of a metal surface that the self-consistent density profile is computed. The effect of the underlying lattice is then reintroduced by means of a first-order pseudopotential calculation, which assumes that the perturbing potential is small.[1] Our results show that this procedure is inadequate for most simple metals.

Consider the striking example of Pb illustrated in Fig. 1(a). The perturbing potential has dips which are of the order of four fifths of the Fermi energy, and its average is close to one third of the bulk value of the effective self-consistent one-body potential from which the density profile is generated in the jellium model. Accordingly the electrons will be strongly attracted inside the metal by such a potential. Earlier jellium treatments[1-4] which included the effect of the ions at most by first-order perturbation theory gave un-

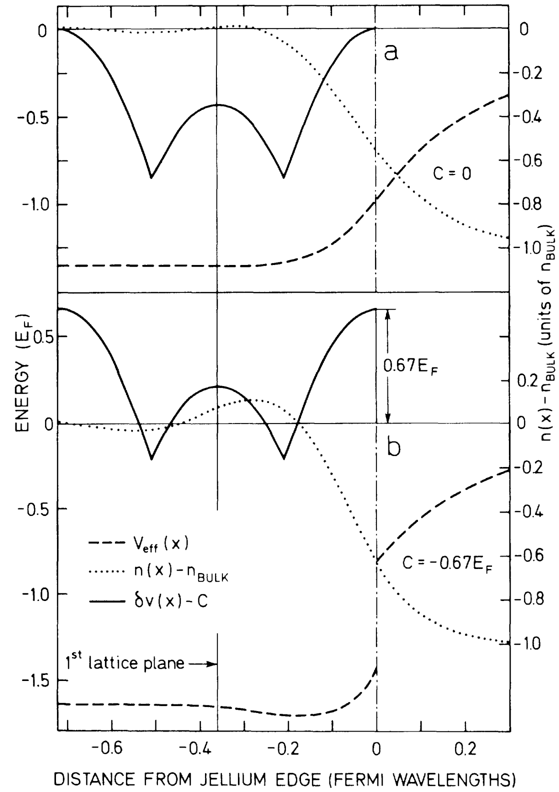

FIG. 1. Self-consistent effective potential $V_{eff}(x)$ shifted to zero value at the vacuum level (dashed line), difference between the self-consistent density profile $n(x)$ and the bulk density n_{bulk} (dotted line), and perturbing potential $[\delta v(x) - C]$ due to pseudopotential lattice effects (solid line) for Pb. (a) Case treated in Ref. 1 (variational parameter C equal to zero); (b) case corresponding to the minimizing value of the variational parameter ($C = C_m = -0.67E_F$). Note how the screening by the electron gas tends to reduce the discontinuity in the effective potential at the jellium edge (dash-dotted vertical line). The distance from the first lattice plane to the jellium edge is equal to one half of the interplanar spacing in the bulk.

realistic density profiles. In addition the first-order correction to the energy[1] was comparable to the unperturbed energy.

We describe a *variational* generalization of the jellium model of metal surfaces which preserves all simplifying features of the latter, but allows the lattice of metal ions to act on the density. The total ground-state energy of a metal occupying the half space $x<0$, and whose ions are described by a local pseudopotential of the form $w(r)=-Ze^2/r+w_R(r)$, where $w_R(r)$ is a repulsive term which cancels the attractive one exactly within a core region of radius r_c, is given by

$$\begin{aligned} E[n] = &\int d^3r \sum\nolimits_l w_R(|\vec{r}-\vec{l}|)n_+(\vec{r}) + E_{\text{Madelung}} + T_s[n] + E_{\text{xc}}[n] \\ &+ \tfrac{1}{2}e^2 \int d^3r \int d^3r' [n(\vec{r} - n_+(\vec{r})]|\vec{r}-\vec{r}\,'|^{-1}[n(\vec{r}\,') - n_+(\vec{r}\,')] + \int d^3r[n(\vec{r}) - n_+(\vec{r})]\delta v(\vec{r}). \end{aligned} \tag{1}$$

Here $n_+(\vec{r})$ is the number density of a fictious positive background [in our case $n_+(\vec{r}) = n_{\text{bulk}}\theta(-x)$, where n_{bulk} is the bulk electronic density]. E_{Madelung} is the electrostatic energy of a lattice of ions of charge Ze at sites $\vec{l}$ ($l_x<0$), neutralized by a charge density $-en_+(\vec{r})$. $T_s[n]$ is the kinetic energy of a noninteracting electron gas of density $n(\vec{r})$, and $E_{\text{xc}}[n]$ is the exchange-correlation energy.[1] $\delta v(\vec{r})$ is the sum over the occupied lattice sites of the ionic pseudopotentials, minus the potential due to the semi-infinite positive background:

$$\delta v(r) = \sum\nolimits_l w(|\vec{r}-\vec{l}|) - e^2 \int_0^\infty d^3r' \frac{n_+(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}. \tag{2}$$

Except for the first term which is purely bulk and the last one which is a pure surface contribution, each separate piece of the energy (1) has a bulk and a surface part. The surface part of E_{Madelung} is the classical cleavage energy.[1] For the remaining three terms (i.e., the jellium contribution), the surface part is obtained by subtracting the corresponding quantities for a uniform system of density n_{bulk} containing the same number of electrons. The correct energy and density are found by minimizing Eq. (1) over all densities $n(\vec{r})$ with $\int d^3r\, n(\vec{r}) = N$ held fixed.

The jellium model is obtained from Eq. (1) by ignoring the last term and minimizing the rest of the energy functional by solving the corresponding 1D single-particle equations self-consistently. The resulting density is then used to evaluate the last term, where the perturbing potential $\delta v(r)$ has been replaced by a suitably taken average[1] $\delta v(x)$ (which vanishes identically outside the metal).

Instead we generate variational wave functions by including a simple potential $C\theta(-x)$ in the single-particle equations. This mimics $\delta v(x)$ and nevertheless guarantees that the single-particle wave functions have the same asymptotic form inside the metal as in the jellium model. To determine the optimum C we first rewrite the pseudopotential lattice contribution to the total energy as

$$\int d^3r[n(\vec{r}) - n_+(\vec{r})]\delta v(\vec{r}) = \int dx[n(x) - n_+(x)]C\theta(-x) + \int dx[n(x) - n_+(x)][\delta v(x) - C\theta(-x)], \tag{3}$$

where the 1D dependence on position has been made explicit. Replacing the last term in (1) by

TABLE I. The surface energy and its components in erg/cm^2 for Pb ($r_s=2.30$, $r_c=1.12$, $Z=4$) and Cs ($r_s=5.63$, $r_c=2.93$, $Z=1$). In Columns 3 to 5 we show the different parts of the jellium contribution to the surface energy, and in column 6 their sum. The terms which are *explicitly* dependent on the structure and face considered are listed in columns 7 and 8, for the particular cleavage plane defined in column 10. The pseudopotential lattice contribution is defined in the text; for a definition of the classical cleavage energy, see Ref. 1. The total surface energy is given in column 9. For each metal the upper line refers to $C=0$ (jellium model) and the lower line to the minimizing value $C=C_m$ of the variational parameter.

Metal	$c\,[E_{\rm F}]$	Kinetic	Coulomb	Exchange-correlation	Jellium subtotal	Pseudo-potential	Classical cleavage	Total	Surface plane
Pb	0.00	−2800	655	1960	−185	930	397	1140	fcc
	−0.67	−820	185	1080	445	−290	397	550	[110]
Cs	0.00	−10	11	70	71	20	12	103	bcc
	0.81	−53	24	119	90	−17	12	85	[110]

TABLE II. Surface energies. The r_s values, pseudopotential core radii r_c, and experimental values for the surface energy are the same as those used in Ref. 1. In each case the minimizing value of the variational parameter and the corresponding energy are given for the most densely packed face ([111] for fcc and [110] for bcc). $\delta\bar{v}$ is the average of the perturbing potential $\delta v(x)$ (see Ref. 1).

						Surface energy (erg/cm^2)		
Metal	Structure	r_s	r_c	$C_m\,[E_F]$	$\delta\bar{v}\,[E_F]$	$C=0$	$C=C_m$	Experiment
Al	fcc	2.07	1.12	-0.16	-0.144	730	645	1000
Pb	fcc	2.30	1.12	-0.67	-0.414	1140	550	620
Li	bcc	3.28	1.06	-0.23	-0.180	375	360	480
Na	bcc	3.99	1.67	0.09	0.011	230	225	230
K	bcc	4.96	2.14	0.21	0.058	139	137	150
Rb	bcc	5.23	2.61	0.61	0.329	122	108	120
Cs	bcc	5.63	2.93	0.81	0.454	103	85	90

the first term of the right-hand side of (3), we can variationally derive single-particle equations which differ from the jellium equations only by the presence of an additional potential $C\theta(-x)$. The density resulting from a self-consistent solution of these equations is then used to evaluate the remainder, i.e., the second term on the right-hand side of Eq. (3). We repeat this procedure for several values of the constant and minimize the *total* energy with respect to C. Since there is no explicit dependence on C in the expression (1) for the total energy, our procedure is simply an efficient way of generating a whole class of densities (of which the one obtained by Lang and Kohn[1] is a particular case, namely the one which minimized the jellium contribution to the surface energy). While our step potential contains no explicit information on the structure, the minimizing value of the step height does depend on the choice of cleavage plane. Accordingly the resulting density profiles, more realistic than those for simple jellium, are appropriate for directly calculating other surface-related properties, such as work functions.

Our calculated density profile for Pb is shown in Fig. 1(b). The density outside the metal is smaller and decays more rapidly than in the jellium case, while sizable Friedel oscillations develop inside. Table I shows the effect of the potential step on the individual components of the surface energy for the two extreme cases of Pb[6] (largest negative C) and Cs (largest positive C). In both cases we observe that the introduction of the constant potential inside the metal leads to a completely different distribution of the jellium part of the surface energy among its three components (kinetic, Coulomb, and exchange-correlation). In Pb the electron density profile is sharpened by the strongly attractive potential, which leads to a lowering of the surface dipole barrier and Coulomb energy. Fewer electrons spill out of the metal, resulting in an increase in kinetic energy and a decrease in exchange-correlation energy.[6] In Cs the opposite effect occurs.

Our results are summarized in Table II and compared with the predictions of the jellium model and with experiment. Note that the minimizing value C_m of the variational parameter roughly mimics the average value $\delta\bar{v}$ of the perturbing potential $\delta v(x)$. The calculated surface energies tend to be slightly smaller than the measured ones. Possibly this defect can be remedied by a nonlocal treatment of exchange and correlation.[7]

This work was done at NORDITA, and it is a pleasure to thank the solid-state group and the staff for their kind hospitality. Particular thanks are due to David Langreth for suggesting a closer examination of the surface energy problem; Risto Nieminen for providing us with his efficient LK program; and John Wilkins for many helpful and encouraging discussions, as well as for his critical reading of the manuscript.

---

*Work supported by National Science Foundation Grant No. DMR 75-09804.

†Work supported in part by the Fonds National Suisse de la Recherche Scientifique.

[1] N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).

[2] N. D. Lang and W. Kohn, Phys. Rev. B 3, 1215 (1971).

[3] N. D. Lang and A. R. Williams, Phys. Rev. Lett. 34, 531 (1975), and to be published; O. Gunnarsson and H. Hjelmberg, Phys. Scr. 11, 97 (1975); O. Gunnarsson, H. Hjelmberg, and B. I. Lundqvist, to be published.

[4] M. Manninen *et al.*, Phys. Rev. B 12, 4012 (1975).

[5] J. Appelbaum and D. Hamann, Phys. Rev. B 6, 2166

(1972); G. Alldredge and L. Kleinman, Phys. Rev. B 10, 553 (1974).

[6] The difference between our jellium result for Pb (-184 erg/cm^2) and the value of 130 erg/cm^2 quoted in Ref. 1 for $r_s = 2.30$ arises from a graphical interpolation used there (N. D. Lang, private communication).

[7] D. C. Langreth and J. P. Perdew, Solid State Commun. 17, 1425 (1975), and to be published.

Surface States on the (001) Surface of Nb†

Steven G. Louie,* Kai-Ming Ho, James R. Chelikowsky,‡ and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720,
and Materials and Molecular Division, Lawrence Berkeley Laboratory,
Berkeley, California 94720

(Received 17 March 1976)

The electronic structure of the (001) ideal surface of niobium is calculated using a self-consistent pseudopotential method. Surface states are identified and analyzed throughout the two-dimensional Brillouin zone. Charge densities and the local density of states near the surface are presented and discussed. Our calculations predict strong surface features in the density of states in the range 0–2 eV above the Fermi energy. Occupied surface states are also discussed.

A self-consistent pseudopotential calculation[1] is presented for the (001) ideal surface of Nb. To our knowledge, this is the first fully self-consistent calculation for a transition-metal surface. The band structure and real space distribution of the electrons near the surface are determined. Surface states of different angular-momentum character are found to exist over a wide range of energies and over different portions of the two-dimensional (2D) Brillouin zone. Our calculations predict strong surface features in the density of states in the range 0–2 eV above the Fermi energy.

Although previous calculations[2-6] have provided useful information about band narrowing and some properties of surface states, their limitations have motivated us to attempt the present calculation. Using a self-consistent pseudopotential method,[1,7] we further take into account the important effects of screening and dehybridization of orbitals at the surface and obtain additional information about surface bands and their $\vec{k}$-space distribution.

In the present calculation, a nine-layer slab of Nb with the (001) surfaces exposed on both sides is used to simulate two noninteracting surfaces. The slab is placed in a periodic superlattice with the slabs separated by a distance equivalent to 6 atomic layers of Nb. Screening is achieved using a Hartree potential derived via Poisson's equation and a Slater-type exchange potential. The only input to the calculation consists of the structure (i.e., the atomic positions) and a fixed ionic pseudopotential for the Nb^{+5} ion cores. The Nb^{+5} ionic potential used here is an l-dependent nonlocal pseudopotential of the form

$$V_p = V(r) + \sum_{l=1}^{2} f_l(r) P_l , \tag{1}$$

where P_l are projection operators for the various angular-momentum components. This potential was obtained by fitting the spectroscopic term values of the Nb^{+4} ion (i.e., the Nb^{+5} plus one-electron system).[8] In addition, we demanded that when V_p was used to calculate the Nb neutral atom self-consistently, it would reproduce the eigenvalues and the positions of the wave-function maxima calculated by Herman and Skillman.[9]

Self-consistent bulk energy-band calculations were carried out to test the Nb^{+5} potential. Plane waves with a maximum reciprocal-lattice vector corresponding to an energy of 10.2 Ry were used in the basis set. This corresponds to about eighty plane waves in the expansion of the eigenfunctions; another eighty plane waves were included by second-order perturbation theory. Since V_{Hartree} and V_{exchange} die quickly in q space, it does not make a significant difference whether the second group of plane waves is used or not in the self-consistency. We do not include these. The s and p levels converge to within 0.01 eV. The d levels shift by at most 0.2 eV if the matrix size is doubled. Good agreement was obtained with previous calculations on bulk Nb.[10] Figure 1 shows the calculated density of states (DOS) evaluated using 112 $\vec{k}$ points in the irreducible part (1/48) of the bcc Brillouin zone together with the DOS from Mattheiss's augmented-plane-wave (APW) calculation.[10] The two curves are in agree-