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# Variational calculations of low-index crystal face-dependent surface energies and work functions of simple metals

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Surface energies and work functions are calculated for the (110), (100), and (111) faces of the bcc metals Li, Ba, Na, K, Rb, and Cs and the fcc metals Al, Pb, Ca, Sr, and for the (0001) faces of the hcp metals Zn and Mg. In the Kohn-Sham energy functional employed, the crystal lattice of ions is represented by the Ashcroft pseudopotential, and nonlocal exchange-correlation energy corrections included via the wave-vector analysis method. The surface energies are determined by application of the Rayleigh-Ritz variational principle. The work functions are obtained for these energy-minimized densities by the variationally accurate, "displaced-profile change-in-self-consistent-field" (DPΔSCF) expression, which is tested for real metals here for the first time. The variational electronic densities employed are those generated by the linear-potential model, which permits the calculations to be primarily analytical. It is observed that the surface energies for each metal with the exception of Rb and Cs increase with decreasing packing density of the exposed crystal face, and that the Smoluchowski rule of decreasing work functions with decreasing packing density is obeyed by each metal except Al and Pb. An analysis of these numerical results indicates them to be superior to those of perturbation theory, and to be equivalent or generally superior to the results of other variational calculations for metals with $r_s \gtrsim 3$. The Mahan-Schaich derivation for the work function of jellium metal is extended to include local ionic pseudopotentials, and the result shown to be equivalent to the DPΔSCF expression. A general expression for polycrystalline work functions is also derived, and an empirical formula given for the work function of alkali metals. It is further argued that it is meaningful, at least for the alkali metals, to compare the polycrystalline work function to the minimum work function, and this equivalence is demonstrated by comparison with experiment.

## I. INTRODUCTION AND FORMALISM

In this paper we present the results of variational calculations of the surface energy and work function for the (111), (100), and (110) faces of the simple metals Al, Pb, Li, Ca, Sr, Ba, Na, K, Rb, and Cs, and the (0001) faces of Zn and Mg. One of the principal advantages of our formalism is that it avoids heavy self-consistent[1] or almost fully self-consistent[2] three- or one-dimensional computations in order to determine these crystallographic face-dependent properties. In fact, for the choice of single-particle wave functions employed in this work,[3,4] the calculations are primarily analytical. Another advantage of this formalism over the self-consistent method is that it may be employed with any explicit density functional for the energy[5] including nonlocal treatments of exchange and correlation, whereas the latter usually requires a local approximation. The approach here is to employ principles that lead to expressions for the physical quantities that are insensitive to deviations of the density from self-consistency. Thus, in addition, the formalism allows a meaningful assessment of the accuracy of the results.

In our calculations for the surface energy $E_s$ we employ the Rayleigh-Ritz variational principle[6] for the energy in conjunction with a Kohn-Sham[7]–type energy functional of the density. The trial electron density profile is uniform in the bulk metal, and its one-dimensional decay at the surface is controlled by a single variational parameter. The variational principle guarantees that the calculated total energy will be an upper bound on the true total energy (for a given energy functional). Since the total energy is the sum of bulk and surface contributions, the calculated surface energy will be an upper bound, with an error that is second order in the error of the trial density, for any system such as jellium[4,8,9] in which the bulk

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density is truly uniform. When this kind of variational trial density is applied to real metals,[10,11] there is no guarantee that the calculated surface energy will be an upper bound, although a reasonable result is still expected on physical grounds for simple metals, where nearly all the bulk binding energy can be accounted for by assuming a uniform bulk density of valence electrons.[10,11] This kind of variational trial density does yield a surface dipole moment that is far superior to that of the jellium model, as shown by an analysis[12] of the work function using the profile-sensitive Koopmans's theorem expression. Thus, if the surface energy is significantly lower in one variational calculation than in another (or in first-order perturbation theory), using the same total energy functional and bulk density in both cases, the former calculation is superior in the sense that it gives a more realistic density.

The surface energy functional of the density $E_s[\rho]$ we consider is

$$\begin{aligned} E_s[\rho] &= E_k[\rho]+E_{es}[\rho]+E_{xc}^{LDA}[\rho]+\Delta E_{xc}^{WV}[\rho] \\ &\quad + E_{ps}[\rho]+E_{cl}[\rho]+E_R[\rho] \ , \end{aligned} \tag{1}$$

where the component $E_k$ is the kinetic energy functional of a system of noninteracting particles, $E_{es}$ is the Hartree electrostatic energy term, $E_{xc}^{LDA}$ the local-density-approximation (LDA) contribution to the surface exchange-correlation energy, and $\Delta E_{xc}^{WV}$ is the nonlocal correction to this term as obtained by the wave-vector analysis method.[13,14] This latter method has been shown[15–17] to be correct both for rapidly varying densities for which a random-phase-approximation calculation exists,[18,19] and for slowly varying densities where it agrees with the density gradient expansion formalism.[20] The alternative substitution of a "local gradient"[20] or "average gradient" correction[16,17] instead is straightforward. The first four terms of Eq. (1) are the "jellium model" contributions[21] to the surface energy. The lattice of ions is included via local pseudopotentials, the difference $\delta v(\vec{r})$ between the pseudopotentials of the semi-infinite crystal and the electrostatic potential of the jellium background giving rise to the pseudopotential $E_{ps}$ and classical cleavage $E_{cl}$ energy contributions.[1] The term $E_R$ is due specifically to the short-range repulsive part of the ionic pseudopotential and must be included only for those crystal faces for which the core radius is greater than half the interplanar spacing. Due to the assumed translational invariance in the plane parallel to the metal surface, each of these components of the surface energy is a functional of the inhomogeneous density $\rho(x)$ which varies in the direction perpendicular to the surface. The definitions of these various functionals are given in Refs. 10 and 11.

We determine the work function $\Phi$ via the "displaced-profile change-in-self-consistent-field" (DPΔSCF) expression.[12,22] This expression is a special case of the change-in-self-consistent-field expression[12]

$$\Phi = \left.\frac{dE_s}{d\Sigma}\right|_{\Sigma=0} \ , \tag{2}$$

where $\Sigma$ is the surface charge density due to the removal of one or more electrons from the metal and the subsequent relaxation of the electron density. Thus the work function is the difference between the surface energies for the infinitesimally charged and neutral surfaces, divided by the infinitesimal surface charge density. For non-self-consistent calculations, it can be shown[12,22] that, in this expression for the work function, the variational parameters that minimize the surface energy for the neutral metal suffice for the charged surface as well. Thus if the class of variational density profiles admits a rigid displacement with respect to the positive background, the density of the charged metal surface may be taken to be that of the neutral surface displaced rigidly relative to the ions by $\Sigma/\bar{\rho}$, where $\bar{\rho}=k_F^3/3\pi^2$ is the average bulk density of the metal. [In terms of the Wigner-Seitz radius $r_s$, the Fermi momentum[23] $k_F=1/\alpha r_s$ where $\alpha^{-1}=(9\pi/4)^{1/3}$.] The result of such a substitution in Eq. (2) is the DPΔSCF expression for the work function

$$\Phi^{DP\Delta SCF}=\Phi_{es}+\Phi_{k+xc}+\Phi_{ps} \ , \tag{3}$$

where $\Phi_{es}$, $\Phi_{k+xc}$, and $\Phi_{ps}$ are the electrostatic, kinetic plus exchange-correlation, and pseudopotential contributions. In the above equation

$$\Phi_{es}=V_{es}(\infty)-V_{es}(a) \ , \tag{4}$$

$$\Phi_{k+xc}=-\epsilon_T \ , \tag{5}$$

$$\Phi_{ps}=\int_{-\infty}^{\infty} dx\, \delta v(x)\frac{d}{dx}\frac{\rho(x)}{\bar{\rho}} \ , \tag{6}$$

where $V_{es}(x)$ is the electrostatic potential due to the electrons and to a neutralizing uniform positive jellium background $\rho_+(\vec{r})=\bar{\rho}\theta(-x+a)$, $\epsilon_T=3k_F^2/10+\epsilon_{xc}(\bar{\rho})$ is the total kinetic plus exchange-correlation[24] energy per electron for the homogeneous electron gas of density $\bar{\rho}$, and $\delta v(x)$ is the planar average of the discrete lattice potential $\delta v(\vec{r})$. Note that the electrostatic term depends only on the electronic density outside the jellium edge $x=a$, whereas $\Phi_{k+xc}$ is a purely bulk contribution. The variational densities to be employed in the determination of $\Phi^{DP\Delta SCF}$ are those which minimize the energy functional of Eq. (1). It is important to note that the $\Phi^{DP\Delta SCF}$ expression is neither a bound nor is it stationary. (However, variational principles[25–27] whereby the density itself and hence the work function are determined correct to second order in the errors of the trial wave function do exist, and have recently been applied[28,29] to the metal surface problem.) The

DPΔSCF expression would be exact if the minimizing density profile for the neutral surface were the exact density. Furthermore, the error $(\Phi^{\rm DP\Delta SCF}-\Phi^{\rm exact})$ should be small since the error in the energy is second order in the error of the trial density. For jellium metal, the DPΔSCF expression for the work function reduces to that previously derived within the local density approximation by Mahan and Schaich,[30] although its accuracy for variationally energy-minimized densities was not at first known. A generalization of the Mahan-Schaich derivation to include local ionic pseudopotentials leading to the same expression for the work function as that of $\Phi^{\rm DP\Delta SCF}$ of Eq. (3) is given in Appendix A.

The expression[10–12] most commonly used for the determination of the work function is the Koopmans's theorem expression $\Phi^{\rm KT}$. For the local ion pseudopotential approximation of the lattice

$$\Phi^{\rm KT}=(\Delta\phi)_r-\mu_T-\langle\delta v\rangle_{\rm av}\ , \tag{7}$$

where $(\Delta\phi)_r=V_{\rm es}(+\infty)-V_{\rm es}(-\infty)$ is the electronic relaxation dipole barrier, $\mu_T=\partial(\bar{\rho}\epsilon_T)/\partial\bar{\rho}$ is the total chemical potential of a uniform electron gas, and $\langle\delta v\rangle_{\rm av}$ is the average value of $\delta v(\vec{r})$ over the volume of the semi-infinite crystal. The explicit mathematical definitions of these terms are also given in Refs. 10 and 11. An expression for $\Phi^{\rm KT}$ including band-structure effects has been derived elsewhere.[11] In this, as in previous[10–12] variational calculations of the work function, these effects are neglected since the bulk can be treated as a region of essentially uniform electronic density, the band-structure contribution to the binding energy being only a small fraction of the total value.[10,11] For fully self-consistent calculations the Koopmans's theorem and DPΔSCF expressions are equivalent. However, if variational energy-minimized densities are employed in the Koopmans's theorem expression, the results for the work function are correct only to the same order as that of the density employed and not correct to second order in the errors of the density as is the energy. Perdew and Sahni[22] have compared DPΔSCF work functions for the jellium surface, using the accurate linear-potential[3,4] trial densities, with the fully self-consistent work functions of Lang and Kohn,[31] and have shown that the errors in $\Phi^{\rm DP\Delta SCF}$ are typically only a few hundredths of an electron volt. The results for the surface energies are also essentially exact.[4,22] The errors in $\Phi^{\rm KT}$, however, are an order of magnitude greater. This same order of magnitude difference in the two sets of results has also been demonstrated for far simpler analytical forms of the trial density.[32,33]

For the crystal lattice of ions we employ the Ashcroft[34] local ion pseudopotential. This pseudopotential leads to accurate theoretical binding energies when compared to experiment[10,11] for all metals (except Li, Ba, and Zn), the difference for the majority being less than 0.3 eV. For K, Ca, and Sr the differences are 0.4, 0.5, and 0.6 eV, respectively. We thus expect our results to be least accurate for Li, Ba, and Zn.

The one-parameter variational electronic single-particle wave functions employed in our calculations are those generated by the linear-potential model.[3,4] The appropriateness of this wave function for surface physics calculations has been amply demonstrated in the literature.[3,4,11,22,35–37] The model leads to semi-analytical expressions[3,11] for the density and the majority of the surface properties of interest. Furthermore, these expressions can be written in terms of universal functions of the field strength parameter $y_F$, and thus the surface properties of a specific metal are easily determined once this parameter is fixed in some physically meaningful manner.

The procedure for the determination of the surface properties is then as follows. For a specific metal and crystal face, we determine the surface energy by minimizing the functional $E_s$ of Eq. (1) employing the variational densities of the linear-potential model. With these energy-minimized densities we then determine the work function via the DPΔSCF expression of Eq. (3). For purposes of completeness we also obtain the Koopmans's theorem results for the work function. We emphasize that these calculations are primarily analytical, e.g., configuration-space integrals have to be performed numerically only for the pseudopotential contributions $\Phi_{\rm ps}$ and $E_{\rm ps}$, and for the LDA value of the surface correlation energy since we employ the Wigner expression[24] for the average correlation energy per particle. The present formalism thus contrasts sharply with other existing calculational methods. For example, the variational surface energy calculations of Monnier and Perdew[10] require the iterative solution of a self-consistent problem for each value of the parameter as it is varied. The face-dependent work-function calculations of Monnier *et al.*[12] (performed for a few metals) within the change-in-self-consistent-field formalism require a fully self-consistent computation for both the neutral as well as an infinitesimally charged surface. The perturbational work-function calculations of Lang and Kohn[31] also require fully self-consistent computations for the neutral and infinitesimally charged surfaces. All these calculations are, however, self-consistent only within the LDA for exchange correlation, whereas the present procedure permits the direct and easy incorporation of nonlocal exchange-correlation effects as obtained from different formalisms.

In Sec. II we present and analyze our results for low-index crystal-face–dependent surface energies and work functions for 12 simple metals as determined by the above formalism. We conclude the paper by discussing possible extensions and improvements to this work.

## II. RESULTS AND ANALYSIS

### A. Surface energies

In Table I we present our results for the surface energy $E_s$ as determined both within the LDA and with the addition of the nonlocal exchange-correlation energy correction. In order to demonstrate the accuracy of our results we first compare our LDA values with those of existing one-dimensional variational and perturbational calculations. We thus include in Table I the variational self-consistent results of Monnier and Perdew[10] (MP) and the perturbational calculations of Lang and Kohn[1] (LK). (The latter calculations employ the density profiles of the jellium surface.) As indicated elsewhere,[10,11] the sign and size of $\langle \delta v \rangle_{\text{av}}$ correlates strongly with the deviations of the density profile from that of the jellium surface. A comparison of the three sets of LDA results can thus be based on an analysis of $\langle \delta v \rangle_{\text{av}}$ and the fraction it is of the Fermi energy for each crystal face, as well as on an evaluation of the different one-electron wave functions employed in each calculation. In Figs. 1 and 2 we plot the values of $\langle \delta v \rangle_{\text{av}}$ for the different crystal faces of the metals considered and note that $\langle \delta v \rangle_{\text{av}}$ decreases as the packing density increases.

In a comparison of our LDA results with those of perturbation theory the following remarks may be made. With the exception of Al (100), and Zn and Mg (0001), our values for the surface energy for all the crystal faces are superior in the sense defined in the introduction. For crystal faces for which $\langle \delta v \rangle_{\text{av}}$ is large (whether positive or negative) and a substantial fraction of the Fermi energy, our results are substantially superior since it is the pseudopotential contribution that is treated perturbationally. For those crystal faces for which $\langle \delta v \rangle_{\text{av}}$ is small or negligible, our results, though superior, are closer to the perturbational values.

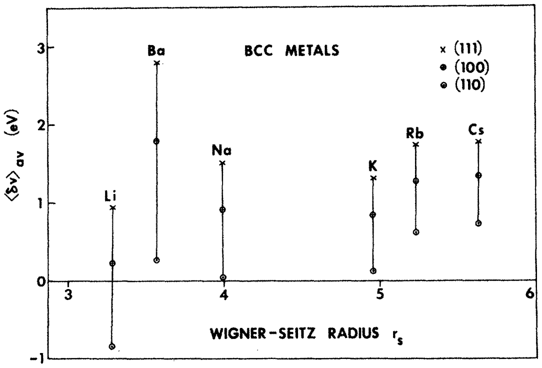

FIG. 1. Low-index crystal-face–dependent values of $\langle \delta v \rangle_{\text{av}}$, the average value of the discrete lattice perturbation over the volume of the semi-infinite crystal, for the bcc metals Li, Ba, Na, K, Rb, and Cs which are represented by their respective values of the Wigner-Seitz radius $r_s$.

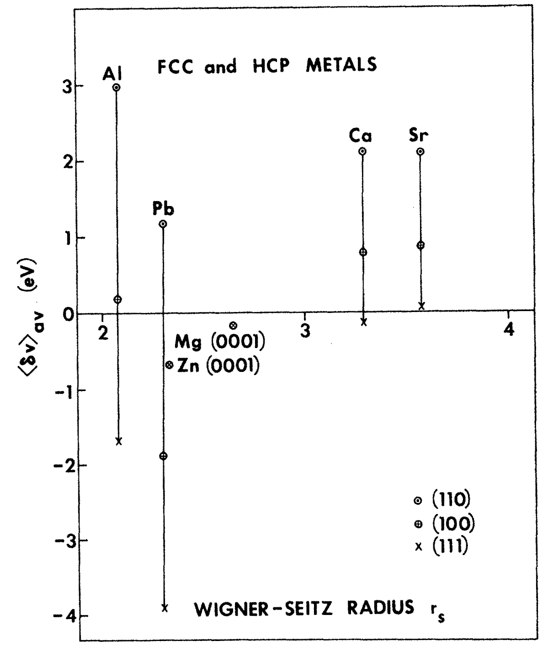

FIG. 2. Low-index crystal-face–dependent values of $\langle \delta v \rangle_{\text{av}}$ for the fcc metals Al, Pb, Ca, and Sr, and hcp metals Zn and Mg.

In a comparison with the variational calculations of MP, we note that for the least densely packed crystal face of all the metals considered, for which the $\langle \delta v \rangle_{\text{av}}$ are positive and large, our results are superior, the improvement increasing with decreasing bulk density. We expect this also to be the case for Ca, Sr, and Ba for which the MP calculations were not performed. For the other crystal faces of the bcc metals the two sets of results are equivalent. On the other hand, the MP surface energies are superior for all the crystal faces where $\langle \delta v \rangle_{\text{av}}$ is large and negative [Al (111) and Pb (100) and (111)], although this superiority is appreciable only for the extreme case of Pb (111), where $\langle \delta v \rangle_{\text{av}}$ is −42% of the Fermi energy. In the Pb (100) face, for which $\langle \delta v \rangle_{\text{av}}$ is substantially negative (see Fig. 2), our result is within 1% of MP. Thus when our energy-minimized linear-potential model density profiles are compared with the MP profiles, the former seem to be more appropriate when $\langle \delta v \rangle_{\text{av}}$ is large and positive, while the latter are preferable when $\langle \delta v \rangle_{\text{av}}$ is large and negative. A possible explanation of this is that, when $\langle \delta v \rangle_{\text{av}}$ is large and positive, the one-electron potential which generates the MP profile has a sharp unnatural dip near the jellium edge (see Fig. 2 of Ref. 10), while the linear-potential model permits a greater electronic

TABLE I. Surface energy $E_s$ results for the low-index crystal faces of 12 simple metals as determined within the local density approximation (LDA), and by inclusion of nonlocal exchange-correlation energy contributions via the wave-vector analysis method. The column $y_F$ represents the energy minimized values of the slope parameter (Ref. 3).

| | | | Surface energies $E_s$ (ergs/cm$^2$) | | | |
|---|---|---|---|---|---|---|
| | | | Local density approximation | | | |
| | | | Variational calculations | | Perturbation theory | Present work with wave-vector correction |
| Metal | Face | $y_F = k_F x_F$ | Present work | Monnier-Perdew[a] | Lang-Kohn[b] | |
| | | | bcc metals | | | |
| Li | (110) | 1.43 | 371 | 358 | 375 | 409 |
| | (100) | 2.12 | 504 | 501 | 503 | 544 |
| | (111) | 2.53 | 666 | 670 | 685 | 707 |
| Ba | (110) | 2.12 | 373 | ... | ... | 401 |
| | (100) | 3.34 | 412 | ... | ... | 441 |
| | (111) | 3.66 | 455 | ... | ... | 484 |
| Na | (110) | 1.48 | 227 | 227 | 229 | 248 |
| | (100) | 2.25 | 248 | 245 | 262 | 271 |
| | (111) | 2.58 | 282 | 321 | 351 | 305 |
| K | (110) | 1.06 | 136 | 137 | 139 | 147 |
| | (100) | 1.76 | 150 | 147 | 159 | 161 |
| | (111) | 2.11 | 164 | 187 | 207 | 176 |
| Rb | (110) | 1.48 | 107 | 108 | 122 | 116 |
| | (100) | 2.27 | 96 | 91 | 115 | 106 |
| | (111) | 2.54 | 73 | 118 | 149 | 83 |
| Cs | (110) | 1.53 | 85 | 85 | 103 | 93 |
| | (100) | 2.32 | 70 | 68 | 92 | 78 |
| | (111) | 2.56 | 42 | 89 | 116 | 50 |
| | | | fcc metals | | | |
| Al | (111) | 2.58 | 692 | 643 | 730 | 852 |
| | (100) | 3.73 | 1530 | 1460 | 1485 | 1701 |
| | (110) | 4.59 | 2836 | 2870 | 3230 | 2964 |
| Pb | (111) | 1.60 | 779 | 550 | 1140 | 886 |
| | (100) | 2.09 | 2186 | 2155 | 2280 | 2298 |
| | (110) | 3.80 | 4866 | 4860 | 4940 | 4990 |
| Ca | (111) | 1.99 | 433 | ... | ... | 472 |
| | (100) | 2.99 | 573 | ... | ... | 615 |
| | (110) | 3.56 | 695 | ... | ... | 737 |
| Sr | (111) | 1.90 | 370 | ... | ... | 401 |
| | (100) | 2.93 | 475 | ... | ... | 507 |
| | (110) | 3.47 | 558 | ... | ... | 591 |
| | | | hcp metals | | | |
| Zn | (0001) | 2.69 | 509 | 478 | 482 | 627 |
| Mg | (0001) | 2.64 | 552 | 541 | 546 | 629 |

[a] See Ref. 10. In Table VII of Ref. 10, the surface energies for the (110) faces of Li, Na, K, and Rb were miscopied; the correct results are given above.

[b] See Refs. 1 and 10.

spillover into the classically forbidden region. When $\langle \delta v \rangle_{av}$ is large and negative the MP effective potential looks more realistic.

With the exception of Pb (111), our LDA surface energies are either nearly equivalent or superior to the variational-self-consistent results of MP, this result being achieved without any need to perform self-consistent calculations. We expect the same accuracy when nonlocal exchange-correlation contributions are added to the total surface energy functional. We also expect our nonlocal exchange-correlation energy results to be superior to those of perturbation theory since our LDA results are superior.

As indicated in the Introduction we include the nonlocal exchange-correlation contributions via the wave-vector interpolation method.[13,14] It has been shown[15] that this correction, although strongly dependent on the bulk density, is essentially independent of the density profile at the surface for a specific metal. The correction may thus be treated as a constant and its value determined for the density which minimizes the LDA value of the surface energy. This has been done for all the various metals and crystal faces, and the results[38] with the addition of this correction are given in Table I and plotted in Figs. 3 and 4. For the bcc metals Li, Ba, Na, and K, and all the fcc metals, the surface energy increases as the packing density decreases. It is only for the two alkali metals Rb and Cs that the reverse is found. Furthermore, for all the bcc metals and the fcc metals Ca and Sr, the greater the bulk density the greater the surface energy for each crystal face. We also note that as the packing density decreases, the value of the variational parameter $y_F$ increases, thus indicating that the density profile is more loosely bound to the surface and has smaller Friedel oscillations for the more loosely packed crystal faces. Indeed we find in Table I that the density profile for real surfaces is essentially decoupled from the average bulk density and depends far more sensitively on the valence and packing fraction; for example, in the alkali metals, which cover a large range of bulk densities, the parameter $y_F$ is always approximately equal to 1.5 for the (100) face and approximately 2.5 for the (111) face. In conclusion, our values for the surface energies indicate that our results are comparable or superior to those of other one-dimensional calculations. Comparisons with experimental surface energies where available have been made elsewhere.[39]

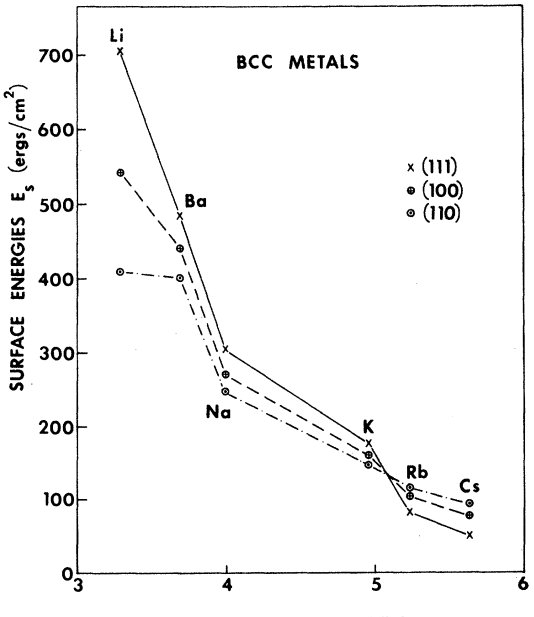

FIG. 3. Low-index crystal-face—dependent surface energies $E_s$ for the bcc metals Li, Ba, Na, K, Rb, and Cs.

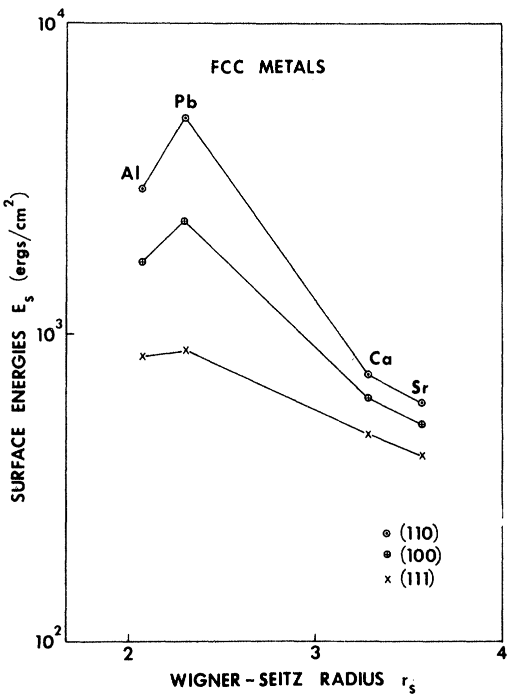

FIG. 4. Low-index crystal-face—dependent surface energies $E_s$ for the fcc metals Al, Pb, Ca, and Sr.

### B. Work functions

In Table II and Figs. 5 and 6 we present our results for the work functions as determined by the DPΔSCF expression. For purposes of completeness and comparison, we also include the results as determined by Koopmans's theorem, the perturbation theory results of Lang and Kohn,[31] the change-in-self-consistent-

TABLE II. Work function $\Phi^{DP\Delta SCF}$ results for the low-index crystal faces of 12 simple metals as determined by the displaced-profile change-in-self-consistent-field (DPΔSCF) expression of Eq. (3). Values for the work function $\Phi^{KT}$ as obtained via the Koopmans's theorem, expression Eq. (7), and the minimum work function $\Phi^{min}$ as defined in Eq. (9) for the alkali metals, are also quoted. The superscript * on a few of the polycrystalline experimental values indicates that these results, though valid, are of unknown reliability because they are not confirmed by any measurements made in recent years with ultrahigh vacuum techniques.

| | | Work functions $\Phi$ (eV) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Present work | | Monnier *et al.*[a] | Perturbation theory[b] | Experiment | | $\Phi^{min}$ |
| Metal | Face | $\Phi^{KT}$ | $\Phi^{DP\Delta SCF}$ | | | Face dependent[c] | Polycrystalline[c] | |
| | | | | bcc metals | | | | |
| Li | (110) | 3.87 | 3.58 | | 3.55 | | | |
| | (100) | 3.47 | 3.30 | | 3.30 | | 2.9* | 3.11 |
| | (111) | 3.20 | 3.16 | | 3.25 | | (3.1)[b] | |
| Ba | (110) | 3.58 | 3.56 | | | | | |
| | (100) | 3.42 | 3.06 | | | | 2.7* | |
| | (111) | 2.85 | 2.86 | | | | | |
| Na | (110) | 3.33 | 3.08 | 3.13 | 3.10 | 2.90[d] | | |
| | (100) | 3.07 | 2.88 | 2.84 | 2.75 | | 2.75 | 2.70 |
| | (111) | 2.79 | 2.75 | 2.76 | 2.65 | | | |
| K | (110) | 3.01 | 2.72 | | 2.75 | | | |
| | (100) | 2.71 | 2.51 | | 2.40 | | 2.30 | 2.39 |
| | (111) | 2.45 | 2.39 | | 2.35 | | | |
| Rb | (110) | 2.72 | 2.49 | | 2.20 | | | |
| | (100) | 2.54 | 2.36 | | 2.10 | | 2.16* | 2.22 |
| | (111) | 2.28 | 2.26 | | 2.05 | | | |
| Cs | (110) | 2.56 | 2.35 | | 2.25 | | | |
| | (100) | 2.40 | 2.23 | | 1.90 | | 2.14 | 2.09 |
| | (111) | 2.14 | 2.14 | | 1.80 | | | |
| | | | | fcc metals | | | | |
| Al | (111) | 3.47 | 3.92 | 4.27 | 4.05 | 4.24 | | |
| | (100) | 4.16 | 4.30 | 4.25 | 4.20 | 4.41 | 4.28 | |
| | (110) | 3.95 | 3.89 | 4.02 | 3.65 | 4.06 | | |
| Pb | (111) | 5.23 | 3.65 | | 3.85 | | | |
| | (100) | 3.88 | 3.81 | 4.10 | 3.95 | | 4.25 | |
| | (110) | 4.08 | 3.84 | 3.90 | 3.80 | | | |
| Ca | (111) | 3.68 | 3.70 | | | | | |
| | (100) | 3.96 | 3.57 | | | | 2.87 | |
| | (110) | 3.43 | 3.20 | | | | | |
| Sr | (111) | 3.57 | 3.61 | | | | | |
| | (100) | 3.82 | 3.42 | | | | 2.59 | |
| | (110) | 3.31 | 3.05 | | | | | |
| | | | | hcp metals | | | | |
| Zn | (0001) | 3.65 | 4.07 | 4.30 | 4.15 | 4.9 | 4.33* | |
| Mg | (0001) | 3.88 | 4.01 | 4.18 | 4.05 | | 3.66* | |

[a] See Ref. 12.

[b] See Ref. 31.

[c] See Ref. 40.

[d] S. Anderson, J. B. Pendry, and P. M. Echenique, Surf. Sci. 65, 539 (1977).

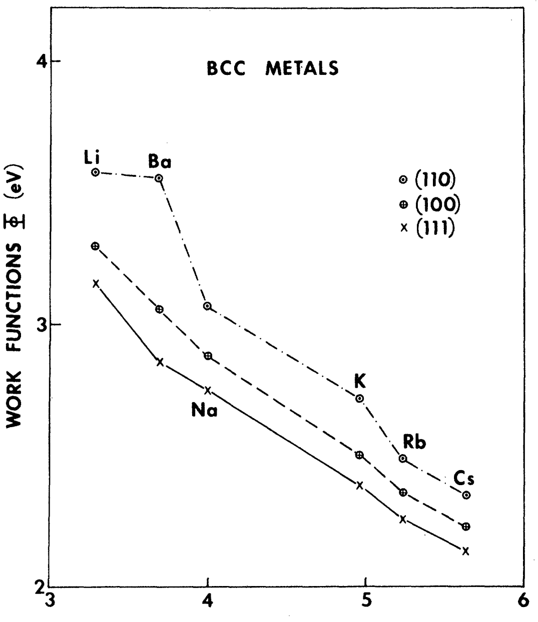

FIG. 5. Low-index crystal-face–dependent work functions Φ for the bcc metals Li, Ba, Na, K, Rb, and Cs.

field theory results of Monnier *et al.*,[12] and polycrystalline and face-dependent experimental results[40] where available. The experimental values quoted have been taken from the most recent compilation and evaluation of such results as performed by Michaelson.[40]

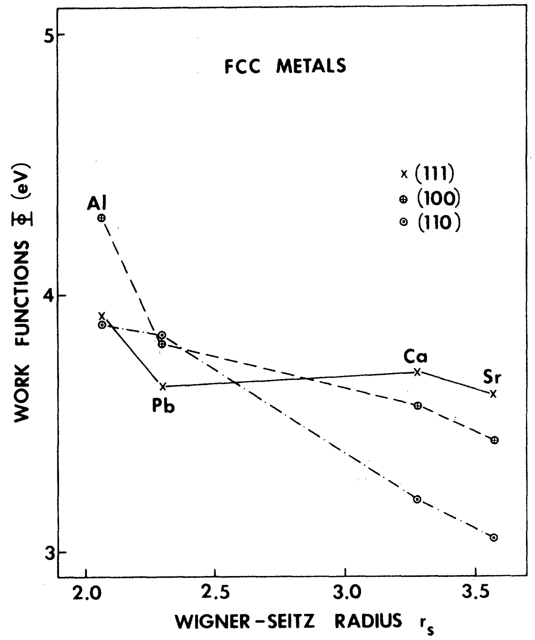

FIG. 6. Low-index crystal-face–dependent work functions Φ for the fcc metals Al, Pb, Ca, and Sr.

We begin with an analysis of the accuracy of our DPΔSCF work functions. For the jellium surface the error[22] is small ($\lesssim 0.05$ eV) for metals with $r_s \geqslant 3$, but rises rapidly to 0.23 eV at $r_s = 2$. The explanation for this behavior can be found in Table I of Perdew and Sahni.[22] The *relative* error of the profile-dependent piece ($\Phi_{es}$) of the DPΔSCF work function is about the same (5%) at $r_s = 2$ as it is at $r_s = 3$, and is considerably larger (15%) at $r_s = 6$. However, the relative contribution of this term to the total work function is 100% at $r_s = 2$, 40% at $r_s = 3$, and only 15% at $r_s = 6$. Thus, although the linear-potential density profiles are actually more realistic for higher densities, where the profile varies more slowly on the scale of the Fermi wavelength, this effect is more than offset by the increase in the relative contribution of the profile-dependent piece of the work function with increasing density. The same considerations should apply for real metals, where the profile-dependent piece ($\Phi_{es} + \Phi_{ps}$) of the DPΔSCF work function is roughly the same as it is for jellium.

Thus for the metals with $r_s < 3$ we believe our results to be less accurate than those of Monnier *et al.*[12] For Mg for which $r_s = 2.65$ it is unclear as to which result is preferable. However, for the metals with $r_s \gtrsim 3$ we believe our DPΔSCF work functions are accurate. The error for $r_s > 3$ is possibly *less* than the 0.05-eV error for jellium, since for most of these metals $\langle \delta v \rangle_{av}$ is positive. Thus for these metals the density profile is more spread out, and the profiles of the linear model are more appropriate, than for jellium.

These conclusions are borne out by the numbers in Table II. For the medium-density metal Na ($r_s = 3.99$) our face-dependent DPΔSCF work functions agree closely (within 0.05 eV) with the change-in-self-consistent-field results of Monnier *et al.*[12] and with the measured polycrystalline value. On the basis of this analysis, we are led to conclude that our work-function results for the alkali metals are probably highly accurate. The perturbation-theory results most closely approximate ours only for the most densely packed (110) faces. This is understandable since for these faces $\langle \delta v \rangle_{av}$ has the least value. For the other faces, the crystal-lattice perturbation effect is not insignificant and the differences in the two sets of results can be as large as 0.34 eV. The Koopmans's theorem values, which are only correct to the same order as the density employed, are consistently greater than the DPΔSCF values.

As may be observed from Fig. 5 for the alkali metals, the work functions decrease with decreasing packing density in agreement with the Smoluchowski[41] rule. In fact, the calculated face-dependent work functions for all the alkali-metal surfaces can be described by the simple empirical rule

$$\Phi = \Phi^{\text{jellium}} - \tfrac{2}{9} \langle \delta v \rangle_{av} , \tag{8}$$

where $\Phi^{\text{jellium}}$ is the work function of jellium at the appropriate $r_s$ value. This expression is in agreement with the Smoluchowski rule, since the less densely packed a crystal face the larger the value of $\langle \delta v \rangle_{\text{av}}$. A nonrigorous though physically plausible argument for Eq. (8) may be obtained by considering the type of variational density employed by Monnier and Perdew.[10] In their work the main effect of $\delta v(\vec{r})$ on the density profile is given by the approximation $\delta v(\vec{r}) \to \langle \delta v \rangle_{\text{av}} \Theta(X + a - x)$ with $X \simeq 0$. The work function within this approximation is given rigorously by Eq. (7). If we write the relaxation surface dipole barrier as $(\Delta\phi)_r = (\Delta\phi)_{\text{jellium}} + \alpha \langle \delta v \rangle_{\text{av}}$, where $(\Delta\phi)_{\text{jellium}}$ is the electrostatic dipole barrier of jellium, then for $X \to -\infty$, $\alpha \to 1$, and for $X \to +\infty$, $\alpha \to 0$. The former case corresponds to the situation where the uniform electron gas perfectly screens the step potential perturbation deep inside the metal, whereas the latter corresponds to the perturbation far outside the crystal where there are no electrons to provide the screening. It seems reasonable, however, that the perturbation near the surface is mostly, though not entirely, screened. Thus we expect $0.5 < \alpha < 1$. Equation (8) is recovered if we choose $\alpha = \frac{7}{9}$.

No comparison of our results with experimental crystal-face–dependent work functions can be made since the latter do not exist. However, it is meaningful, at least for the alkali metals, to compare the minimum work function $\Phi^{\text{min}}$ (which is the least of all face-dependent work functions for a given metal) with polycrystalline experimental values. By cleaving the crystal along a sufficiently high-index face for which the interplanar spacing $d \to 0$, we can estimate[42] $\Phi^{\text{min}}$ from Eq. (8) as

$$\Phi^{\text{min}} = \Phi^{\text{jellium}} - \tfrac{2}{9} \langle w_{\text{R}} \rangle_{\text{av}} \quad , \tag{9}$$

where $w_{\text{R}}$ is the short-range repulsive part of the ionic pseudopotential. The values of $\Phi^{\text{min}}$ thus determined are also quoted in Table II. Whether the above comparison is appropriate depends partly on how the work-function measurement is performed. Consider, for example, the measurement[43] of the photoelectric emission threshold, which is the method by which these experimental results were obtained with the exception of Li where the field emission method was employed. For Li we have also quoted the polycrystalline field emission[43] value for the work function given in Ref. 31. The polycrystalline surface is assumed to be composed of "patches," each patch being a certain cleavage plane of the crystal. Since different cleavages produce different work functions, and since the work function is the negative of the chemical potential measured with respect to the vacuum level, when the surface is created electrons must flow to equalize the chemical potential everywhere. The *average* surface charge density of the metal will remain zero, but some patches will receive a small positive or negative surface charge, which will produce a small but long-range electric field.

First suppose that the photoelectrons are collected at a point which is far from the surface on the scale of the Fermi wavelength, but still close enough that the electrostatic potential from the surface charges is essentially still what it was on the surface at the point of emission. Clearly electrons will first be collected from the faces of the lowest work function, and the polycrystalline work function will be the same as the minimum work function.

Next suppose that instead the photoelectrons are collected at a point so far from the metal that the potential from the surface charge has reached its limiting value, a constant. The energy required to remove an electron from inside the metal to this point is the same for emission through all patches. This polycrystalline work function is an average of the work functions of all exposed patches

$$\Phi^{\text{poly}} = \sum_i f_i \Phi_i / \sum_i f_i \quad , \tag{10}$$

where $\Phi_i$ is the work function of the cleavage corresponding to the $i$th patch. The weights $f_i$ are well defined but not simple (see Appendix B). Under appropriate geometries, such as a plane surface with a periodic pattern of patches, Herring and Nichols[44] have shown that one can use the patch areas $A_i$ as weights.

There are only a few low-index crystal faces, while there are infinitely many high-index crystal faces, and the high-index crystal faces all have essentially the minimum work function. In the alkali metals even the (111) face has a work function within 0.05 eV of the minimum work function (see Table II). Thus we might expect that the average implied for the polycrystalline work function should be only slightly higher than the minimum work function, unless the surface energy of the higher-index faces renders them too unlikely to appear. In the low-density alkali metals the (110), (100), and (111) faces all have essentially the same surface energy and so we expect all faces to be exposed in a polycrystalline sample. Thus it seems appropriate to compare the minimum work functions to the polycrystalline work function, at least for the alkali metals. Such a comparison (see Table II) indicates the two sets of results to be essentially equivalent.

We now analyze the accuracy of our work-function results for the other metals. For the low-density fcc metals Ca and Sr, for which $\langle \delta v \rangle_{\text{av}}$ can be positive and large, and for which our variational densities are ideally suited, we expect our results to be highly accurate. Note (see Fig. 6) that for these metals the Smoluckowski rule is satisfied. For the high-density metals Al, Pb, and Zn our DP$\Delta$SCF results are reliable on the scale of the work function itself (eV's), but probably not on the scale of its face dependence (tenths of an eV), for reasons discussed previously for the jellium surface. For all three faces of Al, our work functions are within 0.3 eV of experiment. In contrast, the three-dimensional variational calculation of Chelikowsky *et al.*[2] for Al (111) led to a work-function value of 5.17 eV, a result which is substantially different from experiment and from the predictions of the various theories quoted here. For the face-dependence of the aluminum work function, the results of Monnier *et al.* compare most favorably with experiment.

The three-dimensional LDA Ashcroft local-pseudopotential calculations of Appelbaum and Hamann[2] lead to a value of 2.71 eV for the work function of Na (100) which is even less in agreement with our work (and that of Monnier *et al.*[12]) than the perturbative results of Lang and Kohn. The 13-atomic-layer-slab-geometry—LDA—nonlocal-pseudopotential calculation of Alldredge and Kleinman[2] gives a value of 3.70 eV for the Li(100) work function. The 0.3-eV difference between this result and that of our work and of perturbation theory (see Table II) is as stated by these authors probably due to the fact that the repulsive and nonlocal part of this pseudopotential is not optimum with respect to the Li band structure as determined by either Callaway[45] or Ham.[46] If the parameter in the repulsive part of the pseudopotential is adjusted so as to match the band gap of Callaway, then these authors obtain a value within 0.1 eV of our results.

In conclusion, we believe our calculations of the face dependence of the work function should be reliable for all the metals with $r_s \gtrsim 3$.

## III. CONCLUSION

In this work we have calculated low-index crystal-face—dependent surface energies and work functions of 12 simple metals. The variational electronic densities employed in our calculations are those generated by the linear-potential model, and nonlocal exchange-correlation energy contributions are included via the wave-vector analysis scheme. The surface energies are determined by application of the Rayleigh-Ritz variational principle, and for these energy minimized densities the work functions are obtained via the variationally accurate DPΔSCF expression. On the basis of the analysis presented in Sec. II, we believe that for the simple metals with $r_s > 3$ our work functions and surface energies are the most accurate of all one-dimensional computational values existing in the literature. For the metals with $r_s < 3$, we continue to prefer the work functions of Ref. 12 and, to a lesser extent, the surface energies of Ref. 10. The trends in our results have been described in Sec. II.

It is, of course, possible to improve on these results, e.g., by employing in the above formalism more accurate variational densities such as those generated within the finite-linear-potential model.[9] The more difficult, but more significant improvement would be to allow for three-dimensional electron density variations. Only small corrections to the results would be obtained by incorporating lattice relaxation effects.[47] It is more important to incorporate improvements in the ionic pseudopotential. The Ashcroft pseudopotential core radii are obtained by fits either to the Fermi surface or transport properties which are not ground-state properties. However, as these pseudopotentials are being employed within the density functional formalism, it appears more appropriate to fit the pseudopotential core radii to measured ground-state properties such as the bulk binding energy or phonon frequencies. The use of such modified Ashcroft pseudopotentials is also under investigation. Finally, a moderate but significant improvement in the calculated surface energies and work functions can be expected when more accurate electron gas correlation energies[48] are used as input to the LDA exchange-correlation energies. In work[3,33] examining different correlation energy expressions for surface physics calculations, it has been observed that work functions are not so sensitive to the choice of correlation, varying only 0.1—0.2 eV from one choice to another, whereas the surface energy results can vary more significantly.

We have recently become aware of work by Bohnen and Ying,[49] and by Rose and Dobson,[50] who have calculated surface energies and work functions allowing for three-dimensional density variations.

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## APPENDIX A: MAHAN-SCHAICH DERIVATION EXTENDED TO REAL METALS

In this appendix we extend a derivation of the work function, originally given by Mahan and Schaich[30] for jellium, to include the crystal lattice via local ionic pseudopotentials. The derivation is simple since it employs the local density approximation for the exchange-correlation *and* kinetic energies, but the results are formally the same as those obtained from the full derivation[12,22] of the DPΔSCF expression for the work function, which does not require any local approximation.

The ground-state energy of a system of $N$ electrons interacting with static ions via a local pseudopotential $w(\vec{r})$ may be written as a functional of the electron density $\rho(\vec{r})$ within the local density approximation as[10]

$$E_N[\rho]=\int d\vec{r}\,\rho(\vec{r})\epsilon_T\{\rho(\vec{r})\}+\int d\vec{r}\,[\tfrac{1}{2}V_{\rm es}(\vec{r})+\delta v(\vec{r})]\rho_T(\vec{r})$$
$$+\left[\int d\vec{r}\sum_{\vec{l}}\omega_{\rm R}(|\vec{r}-\vec{l}|)\rho_+(\vec{r})+\tfrac{1}{2}\int\int d\vec{r}\,d\vec{r}\,'\frac{\rho_+(\vec{r})\rho_+(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right.$$
$$\left.-\int d\vec{r}\sum_{\vec{l}}\frac{z}{|\vec{r}-\vec{l}|}\rho_+(\vec{r})+\tfrac{1}{2}\sum_{\vec{l},\vec{l}'}{}'\frac{z^2}{|\vec{l}-\vec{l}'|}\right], \tag{A1}$$

where

$$\rho_T(\vec{r})=\rho(\vec{r})-\rho_+(\vec{r}) ,$$
$$V_{\rm es}(\vec{r})=\int\frac{\rho(\vec{r})-\rho_+(\vec{r})}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,' ,$$
$$\delta v(\vec{r})=\sum_{\vec{l}}\omega(|\vec{r}-\vec{l}|)+\int d\vec{r}\,'\frac{\rho_+(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} .$$

All the various symbols and terms of Eq. (A1) are defined in the text. Now in order to determine the work function $\Phi$ which is defined[21] as

$$\Phi=[V_{\rm es}(\infty)+E_{N-1}]-E_N , \tag{A2}$$

we need to obtain the difference between the energies of the $N$ and $N-1$ electron systems. From Eq. (A1) we obtain

$$E_N-E_{N-1}=\int d\vec{r}\,\rho_\sigma(\vec{r})\left[\frac{\partial(\rho\epsilon_T)}{\partial\rho}+V_{\rm es}(\vec{r})+\delta v(\vec{r})\right] , \tag{A3}$$

where $\rho_\sigma(\vec{r})$ is the infinitesimal change in the density between the neutral and charged systems when an electron is removed to infinity. [The contributions of the terms within the larger parentheses in Eq. (A1) vanish in Eq. (A3) since they remain unchanged when an electron is thus removed.] If we now choose the same form for $\rho_\sigma(\vec{r})$ as suggested by Mahan and Schaich

$$\rho_\sigma(\vec{r})=-\frac{1}{\bar{\rho}A}\frac{d\rho}{dx} , \quad \int\rho_\sigma(\vec{r})\,d\vec{r}=1 , \tag{A4}$$

where $A$ is the surface area of the sample, and employ the identity[30]

$$\int_{-\infty}^{\infty}dx\left[-\frac{1}{\bar{\rho}}\frac{d\rho}{dx}\right]V_{\rm es}(x)=V_{\rm es}(a) \tag{A5}$$

we have

$$E_N-E_{N-1}=\epsilon_T(x=-\infty)+V_{\rm es}(a)$$
$$+\int_{-\infty}^{\infty}dx\left[-\frac{1}{\bar{\rho}}\frac{d\rho(x)}{dx}\right]\delta v(x) . \tag{A6}$$

Thus

$$\Phi=[V_{\rm es}(\infty)-V_{\rm es}(a)]-\epsilon_T$$
$$+\int_{-\infty}^{\infty}dx\left[\frac{1}{\bar{\rho}}\frac{d\rho(x)}{dx}\right]\delta v(x) \tag{A7}$$

which is identical to Eq. (3) for $\Phi^{\rm DP\Delta SCF}$.

## APPENDIX B: POLYCRYSTALLINE WORK FUNCTION

Consider a sample with plane crystal faces labeled by the index $i$. The total energy $E$ of this sample may be written as

$$E=\epsilon\Omega+\sum_i A_i\left[E_{s,i}+\Phi_i\Sigma_i+\tfrac{1}{2}\sum_j X_{ij}\Sigma_i\Sigma_j\right] , \tag{B1}$$

where $\Omega$ is the volume and $\epsilon$ the bulk energy density. For the facet $i$, $A_i$ is the surface area, $\Sigma_i$ the surface charge density, $E_{s,i}$ the surface energy when $\Sigma_i=0$, and $\Phi_i=dE_{s,i}/d\Sigma_i|_{\Sigma_i\to 0}$ is the work function when $\Sigma_i=0$. The $X_{ij}$ arise from long-range electrostatic interactions and so may depend in a complicated way on the size and shape of the sample. However, $E_{s,i}$, $\Phi_i$, and $X_{ij}$ are independent of the $\Sigma_i$. The $\Sigma_i$ are determined by minimization of the energy $E$ subject to the constraint that the total surface charge

$$Q=\sum_i A_i\Sigma_i=0 . \tag{B2}$$

On introducing a Lagrange multiplier $\Phi$, the result of the variational minimization

$$\delta(E-\Phi Q)=0 \tag{B3}$$

or equivalently

$$\frac{d}{d\Sigma_i}\left[E-\Phi\sum_i A_i\Sigma_i\right]=0 , \tag{B4}$$

is

$$\sum_i X_{ij}\Sigma_j=\Phi-\Phi_i , \tag{B5}$$

from which, employing the identity

$$\sum_i(X^{-1})_{ki}(X_{ij})=\delta_{kj} , \tag{B6}$$

we obtain

$$\Sigma_i = \sum_j (X^{-1})_{ij}(\Phi - \Phi_j) \ . \tag{B7}$$

Substituting Eq. (B7) for $\Sigma_i$ into Eq. (B2) leads to

$$\Phi = \sum_j f_j \Phi_j / \sum_j f_j \ , \tag{B8}$$

where

$$f_j = \sum_i A_i (X^{-1})_{ij} \ . \tag{B9}$$

The Lagrange multiplier $\Phi$ can easily be identified as the work function[12] since from Eq. (B3) $\Phi = dE/dQ$.

For simplicity our derivation of (B8) has assumed a uniform (or lattice periodic) surface charge density on each facet. The same derivation can be made if the surface charge density varies slowly over each facet, i.e., if each facet can be divided into portions, large on the microscopic scale, over which the surface charge density is essentially uniform.

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

[2] See, e.g., J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 6, 2166 (1972); G. P. Alldredge and L. Kleinman, *ibid.* 10, 559 (1974); J. R. Chelikowsky, M. Schlüter, S. G. Louie, and M. Cohen, Solid State Commun. 17, 1103 (1975); J. G. Gay, J. R. Smith, and F. J. Arlinghaus, Phys. Rev. Lett. 38, 561 (1977); C. S. Wang and A. J. Freeman, Phys. Rev. B 19, 793 (1979).

[3] V. Sahni, J. B. Krieger, and J. Gruenebaum, Phys. Rev. B 15, 1941 (1977).

[4] V. Sahni and J. Gruenebaum, Solid State Commun. 21, 463 (1977).

[5] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[6] B. L. Moisewitsch, *Variational Principles* (Interscience, New York, 1966), p. 153.

[7] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[8] G. D. Mahan, Phys. Rev. B 12, 5585 (1975).

[9] V. Sahni, C. Q. Ma, and J. S. Flamholz, Phys. Rev. B 18, 3931 (1978).

[10] R. Monnier and J. P. Perdew, Phys. Rev. B 17, 2595 (1978); J. P. Perdew and R. Monnier, Phys. Rev. Lett. 37, 1286 (1976); Phys. Rev. B 22, 1124(E) (1980).

[11] V. Sahni and J. Gruenebaum, Phys. Rev. B 19, 1840 (1979).

[12] R. Monnier, J. P. Perdew, D. C. Langreth, and J. W. Wilkins, Phys. Rev. B 18, 656 (1978).

[13] D. C. Langreth and J. P. Perdew, Solid State Commun. 17, 1425 (1975).

[14] D. C. Langreth and J. P. Perdew, Phys. Rev. B 15, 2884 (1977).

[15] J. P. Perdew, D. C. Langreth, and V. Sahni, Phys. Rev. Lett. 38, 1030 (1977).

[16] D. C. Langreth and J. P. Perdew, Solid State Commun. 31, 567 (1979).

[17] D. C. Langreth and J. P. Perdew, Phys. Rev. B 21, 5469 (1980).

[18] J. Harris and R. O. Jones, J. Phys. F 4, 1170 (1974). See also Ref. 36.

[19] E. Wikborg and J. E. Inglesfield, Solid State Commun. 16, 335 (1975).

[20] D. J. W. Geldart and M. Rasolt, Phys. Rev. B 13, 1477 (1976); M. Rasolt and D. J. W. Geldart, Phys. Rev. Lett. 35, 1234 (1975); Solid State Commun. 18, 549 (1976).

[21] N. D. Lang, Solid State Phys. 28, 225 (1973).

[22] J. P. Perdew and V. Sahni, Solid State Commun. 30, 87 (1979).

[23] Atomic units are used: $|e| = \hbar = m = 1$. The unit of energy is 27.21 eV.

[24] In this work we employ the Wigner interpolation formula $\epsilon_c = -0.44/(r_s + 7.8)$ atomic units for the correlation energy per electron.

[25] J. B. Krieger and V. Sahni, Phys. Rev. A 6, 919 (1972).

[26] V. Sahni and J. B. Krieger, Phys. Rev. A 6, 928 (1972).

[27] V. Sahni and J. B. Krieger, Phys. Rev. A 8, 65 (1973).

[28] C. Q. Ma and V. Sahni, Solid State Commun. 27, 1193 (1978).

[29] C. Q. Ma and V. Sahni, Phys. Rev. B 22, 1843 (1980).

[30] G. D. Mahan and W. L. Schaich, Phys. Rev. B 10, 2647 (1974).

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

[32] V. Sahni and C. Q. Ma, Phys. Rev. B 20, 3511 (1979).

[33] J. P. Perdew, Phys. Rev. B 21, 869 (1980).

[34] N. W. Ashcroft, Phys. Lett. 23, 48 (1966).

[35] C. Q. Ma and V. Sahni, Phys. Rev. B 16, 4249 (1977).

[36] C. Q. Ma and V. Sahni, Phys. Rev. B 20, 2291 (1979).

[37] V. Sahni and C. Q. Ma, Phys. Rev. B 22, 5987 (1980).

[38] In the work of Monnier and Perdew (Ref. 10), nonlocal exchange-correlation contributions to $E_s$ were also included for the majority of metals considered here but only for the most densely packed crystal faces. A detailed comparison of these results with ours for these crystal faces is given in Ref. 11. With the exception of the Pb (111) face, the two sets of results are equivalent.

[39] A comparison between our sets of results for the most densely packed crystal faces and those of liquid surface tension measurements and other experimental results is made in Ref. 11. A paper [A. H. Maitland and G. A. Chadwick, Philos. Mag. 19, 645 (1969)] has been brought to our attention which quotes an experimental value of 575 ergs/cm$^2$ for the surface energy of Zn (0001). This result is substantially different from the experimental values given in Ref. 11, but closely approximates our theoretically determined result.

[40] H. B. Michaelson, J. Appl. Phys. 48, 4729 (1977).

[41] R. Smoluchowski, Phys. Rev. 60, 661 (1941).

[42] The explicit expression for $\langle \delta v \rangle_{\mathrm{av}}$, the average of the discrete lattice perturbation $\delta v(\vec{r})$ over the volume of the semi-infinite crystal, is $\langle \delta v \rangle_{\mathrm{av}} = \langle w_{\mathrm{R}} \rangle_{\mathrm{av}} - \pi \bar{\rho} d^2/6$ where $\langle w_{\mathrm{R}} \rangle_{\mathrm{av}} = 2\pi \bar{\rho} r_c^2$.

[43] J. M. Blakeley, *Introduction to the Properties of Crystal Surfaces* (Pergamon, New York, 1973).

[44] C. Herring and M. H. Nichols, Rev. Mod. Phys. 21, 185 (1949).

[45] J. Callaway, Phys. Rev. 124, 1824 (1961); 131, 2839(E) (1963).

[46] F. S. Ham, Phys. Rev. 128, 82, 2524 (1962).

[47] J. P. Perdew and R. Monnier, J. Phys. F 10, L287 (1980).

[48] D. Ceperley, Phys. Rev. B 18, 3126 (1978).

[49] K. -P Bohnen and S. C. Ying, Phys. Rev. B 22, 1806 (1980).

[50] J. H. Rose and J. F. Dobson, Solid State Commun. 37, 91 (1981).