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Calculated Electronic Profiles for Liquid-Metal Surfaces

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The electronic density profile for a liquid-metal surface can be calculated by solving the self-consistent Lang-Kohn equations for the electronic wave functions. One requires a surface density profile for the ion cores, which enters the electrostatic and pseudopotential parts of the electronic Hamiltonian. We use oscillatory profiles, suggested by those found by molecular-dynamics simulations on a pseudoatom model. Calculating surface potentials and work functions, we obtain excellent agreement with experiment (within 0.2 eV). It is shown that use of either step-function ion profiles or a simple variational method leads to serious errors (1–2 eV) for these quantities.

I. INTRODUCTION

Understanding the density of conduction electrons at a liquid-metal surface, and how it responds to change in environment and to charging, may be important to formulation of realistic models[1] for the common electrochemical interface. These electrons contribute to the difference in electric potential across the planar interface according to

$$\chi_m = -4\pi \int_{-\infty}^{\infty} dz \int_{-\infty}^{z} dz'[Z\rho_+(z') - \rho_-(z')] , \quad (1)$$

where $Z\rho_+(z)$ is the charge-density profile of the positive ion cores and $\rho_-(z)$ that of the conduction electrons (a simple metal, with separation of core and valence bands, is assumed).[2] Atomic units are used throughout.

The profile $\rho_+(z)$ should be obtained by a statistical mechanical averaging over ion configuration, the ions interacting by a potential which includes screening by the conduction electrons.[3] To each ion configuration there corresponds an electron density; averaging these densities over ion configurations produces $\rho_-(z)$. Since the interionic potential includes the interaction of each ion with the perturbation in electron density caused by the others, a complete calculation for the liquid-metal surface requires the generation of new interionic potentials, dependent on the electronic distribution, for each ionic configuration until consistency between ionic and electronic profiles is obtained. Calculation of the electronic profile and such properties as the surface potential for a particular ionic distribution is much less difficult.

The average value of a surface property, which should in principle be derived from a series of calculations for different ionic distributions, may be estimated from a single calculation for a single ionic distribution. This distribution should not differ much from the average profile $\rho_+(z)$. Assuming some ionic profile, one can calculate a surface potential and work functions to compare with experiment. If this property is sensitive to the ionic profile, agreement with experiment is a test of the quality of the profile. Thus, we assume[2] that $\rho_-(z)$ can be obtained from a single calculation, using the average profile $\rho_+(z)$ for the ions. Previous calculations[4,5] assumed a step function or other forms for $\rho_+(z)$. Furthermore, $\rho_-(z)$ was obtained[2,4] by a variational method based on local-density-functional theory,[6] with a simple form for the trial function.

Recently, however, ion profiles have been calculated by D'Evelyn and Rice[7] from Monte Carlo simulations based on a pseudoatom theory, and we have used[8] the profile $\rho_+(z)$ for mercury to generate $\rho_-(z)$ and thence χ_m. A pseudoatom theory[9] by itself cannot generate charge densities, as it implies local neutrality, but when $\rho_+(z)$ for the pseudoatom theory was used in a separate calculation to obtain $\rho_-(z)$ we found[8] very satisfactory results for mercury, as evidenced by comparison of calculated work functions to experimental results. In addition to the use of the D'Evelyn-Rice profile, our calculation used the self-consistent (Lang-Kohn) equations[10] instead of a variational method. Even for the step-function profile, this led to a significant change in χ_m.

Below, we report results for several of the metals for which variational calculations with a step-function ion profile were previously reported. We calculate χ_m and the work functions, to assess (1) the accuracy of the variational theory for the step-function profile and (2) the effect of using a highly oscillatory ion profile such as that used for mercury. It will be seen that the fair agreement with experimental work functions previously obtained[4] becomes poor when self-consistent calculations replace variational methods, but becomes very good when the oscillatory ion

profile is introduced. The work function is thus sensitive to the ion profile and should indicate its quality.

II. CALCULATIONS

The work function Φ may be written as a sum of two contributions:

$$\Phi = \mathcal{X}_m - \mu_e . \qquad (2)$$

Here, $\mathcal{X}_m$ is the value of the electrostatic potential far inside the metal minus the value far outside, while μ_e, sometimes called the chemical potential, is the energy per electron at the top of the conduction band, relative to the bottom of the band. Since there are no fields in the bulk metal or in the vacuum outside, $\mathcal{X}_m$ is a surface property and μ_e a bulk property.

The Hamiltonian for the electrons includes the kinetic and Coulomb energies, calculated exactly (see below), the exchange and correlation energies, which are represented by a local density-dependent potential, and the interaction between electrons and ion cores. The last interaction is represented by an energy-independent local model potential of the Heine-Abarenkov form,

$$V_{EI} = -Z/r , \quad r > R_m$$
$$V_{EI} = ZA_0 , \quad r \le R_m \qquad (3)$$

where the values of the pseudopotential core radius R_m and the core constant A_0 are those previously used,[4,11] and given in Table I, and Z is the ionic charge. The exchange-correlation energy density is given by $V_{xc}\rho$, where ρ is the local electron density and the exchange-correlation potential is[12]

$$V_{xc}(\rho) = \frac{-0.458}{r_s} - \frac{0.44}{r_s + 7.8} , \qquad (4)$$

where

$$4\pi r_s^3 \rho / 3 = 1 . \qquad (5)$$

Therefore, the bulk term in the work function is

$$\mu_e = 1.8416 r_b^{-2} - 0.6107 r_b^{-1}$$
$$- 0.44(7.8 + 4r_b/3)(7.8 + r_b)^{-2}$$
$$+ 2\pi R_m^2 \rho_b (1 - \tfrac{2}{3} | A_0 | R_m) , \qquad (6)$$

there being no electrostatic contribution. Here, ρ_b is the bulk electron density and r_b is calculated from ρ_b according to (5). The first term in (6) is the kinetic-energy part, representing the sum of the kinetic energies of spin orbi-

tals which are occupied by electrons.

The contributions to μ_e are given in Table I. It should be noted that a different exchange-correlation functional was used in our earlier work,[4] which gave

$$- 1.5873 r_b^{-1} - 0.07007 - 0.005167 \ln\rho_b$$

instead of the second and third terms in (6). As shown in Table I, the results are only slightly changed, but, since the corresponding V_{xc} was used in determining the electron density, Eq. (6) should be used with the $\mathcal{X}_m$ calculated from Lang-Kohn calculations. The Thomas-Fermi density functional used for kinetic energy gives the same contribution to μ_e as the correct summing over eigenfunctions.

The variational calculations require that all contributions to the electronic energy be expressed as a local density functional. Then, assuming a form for the electronic density profile $\rho(z)$, we vary[13] parameters in it to minimize the surface energy. The one- and two-parameter forms used[2,4] were monotonic. Thus when variation is replaced by a self-consistent solution of the integro-differential equations for electron orbitals, different (and presumably better) results will be obtained because the density functional used for the kinetic energy $(\kappa_k \rho^{5/3})$ is not sufficiently accurate and because the variational function is not sufficiently flexible. The self-consistent calculation proceeds as follows: We obtain eigenvalues and eigenfunctions from the Schrödinger equation

$$- \tfrac{1}{2} \nabla^2 \Psi - V(z)\Psi + [\delta(\rho V_{xc})/\delta\rho]\Psi + V_{ps}\Psi = E\Psi , \qquad (7)$$

where V is the electrostatic potential, determined from ρ_+ and ρ_-, and

$$V_{ps}(\mathbf{r}) = Z \int d\mathbf{r}' \rho_+(z')(A_0 + s^{-1})\Theta(R_m - s) \qquad (8)$$

with $s = |\mathbf{r} - \mathbf{r}'|$, is the difference between the ion-electron pseudopotential and a purely Coulomb interaction, averaged over the profile ρ_+. Combining the squared eigenfunctions of (7) with eigenvalues below the Fermi level E_F [$E_F = (\tfrac{1}{2})k_F^2$ with $\rho_b = k_F^3/3\pi^2$], we obtain an electron density $\rho_-(z)$. At self consistency, this density should be identical to the electron density used in constructing the Hamiltonian of (7). Our method for achieving this is discussed elsewhere.[14]

The ion profiles we used are based on those found by D'Evelyn and Rice for mercury[7] and cesium.[15] They are highly oscillatory within the metal and drop rapidly to zero outside the surface (metal-insulator transition):

$$\rho_+(z) = Z^{-1}\rho_b[1 - ae^{\alpha z}\cos(\beta z)] , \quad z < Y . \qquad (9)$$

TABLE I. Bulk properties (a.u.).

Metal	Electron density	Pseudopotential parameters R_m	A_0	Kinetic energy	Exchange correlation	Old exchange correlation	Pseudopotential
						Contributions to μ_e	
Hg	0.01267	2.6	−0.485	0.2601	−0.2751	−0.2771	0.0857
In	0.01711	2.4	−0.440	0.3178	−0.3002	−0.3028	0.1833
Ga	0.02283	2.4	−0.490	0.3851	−0.3265	−0.3299	0.1785
Al	0.02695	2.0	−0.460	0.4302	−0.3428	−0.3466	0.2619

Here, $Z^{-1}\rho_b$ is the ion density in the bulk metal, $a^{-1}=e^{\alpha Y}\cos(\beta Y)$, and

$$\beta\tan(\beta Y)=-\alpha+Y(\alpha^2+\beta^2)$$

fixes the center of positive charge at 0, i.e.,

$$\int_{-L}^{\infty}dz\rho_+(z)=L\rho_b$$

for large L. The parameter α governs the width of the profile, but previous calculations[8] showed results were insensitive to its value, so we have used $\alpha=\frac{1}{2}$ in all cases. The wavelength of the oscillations is governed by β. For mercury, we chose $\beta=1.225$ to fit the profile given[7] by D'Evelyn and Rice. For the other metals, we took $\beta=2k_F$, corresponding to the wavelength of the Friedel oscillations ($2k_F=1.444$ for mercury), expecting results to be relatively insensitive to this parameter as well.

In Table II we give first the experimental work functions Φ for the four metals considered, and then the results for μ_e, χ_m, and Φ obtained[4] previously, by variational calculations with a step-function profile for the ions. Following that, we give the values for these quantities that result from a self-consistent calculation, again with a step-function profile (the slight change in μ_e is due to the changed exchange-correlation energy functional, mentioned above). It is seen that the fair agreement we had[4] with experimental and calculated work functions is destroyed. The average deviation between experimental and calculated work functions goes from 0.6 to 1.3 eV, the change being greater for the metals of higher electron density.

When the oscillatory profiles with $\alpha=0.5$ and $\beta=2k_F$ (except for mercury) are used, there is a large increase in χ_m over that for the step-functions. The average deviation between experimental and calculated work functions is reduced to about 0.16 eV. Furthermore, Φ(calculated) is too high for In, Ga, and Al. For mercury, the profile of D'Evelyn and Rice provided the value of β, which was somewhat below $2k_F$ (1.255 instead of 1.44), and Φ(calculated) is slightly low. For the case of Cs, $\rho_b=0.0012341$ gives $2k_F=0.6637$, whereas the Monte Carlo simulations[15] give a profile with β about 0.62; for Na, $2k_F=0.9478$ and the simulations make β about 1.0, slightly larger. It seems reasonable that the actual profiles for the other metals correspond to lower values of β and would bring Φ(calculated) closer to experiment, or perhaps below.

In Fig. 1 we show part of the ion and electron profiles for aluminum. Those for the other metals resemble this one. The oscillations in ρ_- follow those in ρ_+ in position, but not in magnitude, except for the large tail of ρ_- ex-
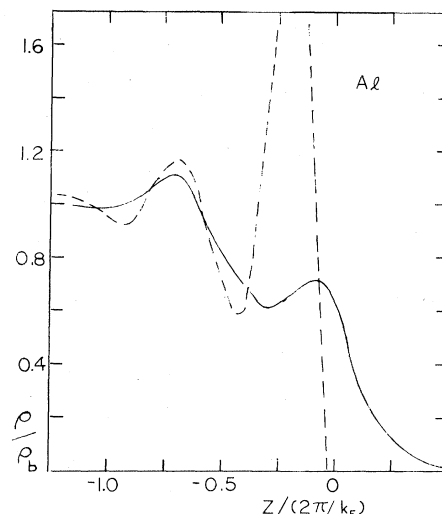

FIG. 1. Surface density profiles for aluminum metal. Solid curve is the electronic profile, dashed curve the ionic profile.

tending into the vacuum. The first and highest maximum in ρ_+ occurring on the tail of ρ_-, there is a substantial oscillation on the rapidly decreasing ρ_- here. Note that self consistency between ionic and electronic profiles does not imply coincidence between them; such coincidence, predicted by certain electrostatic models, implies a vanishing surface potential. Indeed, it has been argued[15] that monotonic profiles for ions and electrons violate self-consistency, since a monotonic electronic profile could produce one-body forces on the ions which would lead to oscillations in their distribution.

III. CONCLUSIONS

The variational method and trial functions employed previously[4] are not good enough to reproduce the results of the self-consistent calculation for the electrons in the presence of a step-function ion profile. The fair agreement between the work functions obtained from the variational method and from experiment is due to a cancellation of errors. The use of the self-consistent method shows that the variational method, either because of the density functional or because of the trial function, is inadequate. The values of the work functions with a step-function profile are actually several volts below experimental values. Changes in pseudopotential or other parameters in the model cannot resolve the discrepancy, as results are insensitive to their values.

TABLE II. Results.

Metal	Experimental work function Φ (eV)	Step-function by variation			Step-function by differential			Oscillatory profile by differential equations		
		μ_e (a.u.)	χ_m (eV)	Φ (eV)	μ_e (a.u.)	χ_m (eV)	Φ (eV)	μ_e (a.u.)	χ_m (eV)	Φ (eV)
Hg	4.50	0.0687	5.37	3.50	0.0707	5.24	3.32	0.0707	6.18	4.26
In	4.16	0.1983	9.05	3.65	0.2009	7.79	2.32	0.2009	9.70	4.24
Ga	4.25	0.2337	10.51	4.15	0.2371	9.48	3.03	0.2371	10.85	4.40
Al	4.20	0.3455	13.92	4.52	0.3493	12.89	3.39	0.3493	13.80	4.30

Going over to an oscillatory profile like (9), however, brings calculated work functions into agreement with experiment. We have shown that an educated guess at the parameters can be made, or at least that, once a profile of the form (9) has been chosen, the exact values of the parameters do not matter much. Given a guess for the ion profile at a liquid-metal surface or, better, an ion profile calculated from a pseudoatom or other model, we can calculate the electron profile and electrostatic properties. Agreement with experiment is good. These results tend to support the existence of spatial oscillations in the average ionic profile at a liquid-metal surface.

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