Theor Chim Acta 68:197-210 (1985)

THEORETICA CHIMICA ACTA

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Conduction electrons of the metal in the electrochemical interface

Jerry Goodisman

Department of Chemistry, Syracuse University, Syracuse, New York 13210, USA

(Received January 2, revised April 10, 1985)

We calculate the conduction electron density profile for a liquid metal in contact with a layer of water molecules, representing the electrolyte phase of an electrochemical interface. The self-consistent Kohn–Sham equations are solved in the absence, and presence, of the electrolyte phase. Results are compared to those from variational calculations, showing that the latter are not sufficiently accurate for this problem. In the potential representing the interaction of the conduction electrons with the water molecules, the contribution of the exchange-correlation potential is extremely important, as well as the constraint of orthogonality to the closed shells of the water, represented by a repulsive pseudopotential. Different exchange-correlation potentials are investigated. Results are quite sensitive to the choice made and to the representation of the pseudopotential. The additional information needed to place these calculations on a firmer basis is indicated.

Key words: Liquid metal — Surface profile — Electron density

1. Introduction

The typical electrochemical interface is the region between a liquid metal (electronic conductor) and an electrolyte (ionic conductor). Although such systems have been much studied, experimentally and theoretically, for a century, it is only recently that the role of the metal phase has been considered in any detail. Experimentally, one cannot separate the contributions of metal and electrolyte phases to the properties of the interface, but it is evident that the electrical potential at any point in the interface is a sum of metal and electrolyte contributions. We are interested in the potential difference across the interface and how it is changed by the presence of the electrolyte phase and by charging. (We are concerned with the polarizable interface, i.e. one for which the electrical potential difference between the phases can be changed without producing a continuous current [1].) One knows from work functions that, because of the separation of charge between conduction electrons and ion cores, there is a surface potential of several volts [2] at a metal surface, so a potential drop of this size with origin in the metal must also exist at the metal-electrolyte interface.

Recent calculations [3-5] have modeled the effect of an aqueous electrolyte phase on the conduction electrons by an effective potential, and obtained the electron density profile by variational calculations. Two aspects of this procedure are questionable and are examined in the present work: the approximtions involved in the variational procedure, and the choice of effective potential. We do not consider whether the effect of the electrolyte phase can be represented at all by a local potential, although this assumption also could be called into question.

With respect to the variational method, there are two issues: the justification of the variational principle used and the adequacy of the variational trial function. Assuming that it is indeed sufficient to treat the conduction electrons in the field of the metal ion cores (plus eventually the field of the electrolyte ions and molecules), one should obtain the conduction electron density $\rho(z)$ from the electronic wave functions. If each of the wave functions up to the Fermi energy ε_F is filled with two electrons,

$$\rho(z) = 2 \int_0^{\varepsilon_F} d\varepsilon \int d^2K |\psi_{\varepsilon,K}|^2 \tag{1}$$

where $\psi_{\varepsilon,K}$ is determined from a one-electron Schrödinger equation, involving some sort of self-consistent field potential. To obtain $\rho(z)$ variationally, and not deal with the $\psi_{\varepsilon,K}$, one must express the electronic energy as a functional of the electron density alone. Some contributions to the total energy can often be well approximated by local functionals of ρ, but not the kinetic energy. The inadequacies of substitution of the Thomas-Fermi density functional [6]

$$E_k^{\mathrm{TF}} = (3h^2/10m_e)(3\pi^2)^{2/3} \int \rho^{5/3}\, d\tau$$

for the kinetic energy in terms of the one-electron wave functions

$$E_k^{ex} = -(h^2/2m_e) \int_0^{\varepsilon_F} d\varepsilon \int d^2K \int d\tau\, \psi_{\varepsilon,K}^*(r) \nabla^2 \psi_{\varepsilon,K}(r)$$

are well-documented [7], and there have been many attempts at improving on this form. Nevertheless, Smith [8] showed that for solid metal surface problems, variational calculations based on E_k^{TF} gave density profiles and potential differences close to those obtained from calculations using E_k^{ex}. A second problem is the choice of trial function, which contains one or more parameters whose values are varied to minimize the electronic energy. A simple one-parameter form such as

$$\begin{aligned} \rho &= \rho_e(1-\tfrac{1}{2}\,\mathrm{e}^{\alpha z}), \qquad z<0 \\ &= \rho_e(\tfrac{1}{2}\,\mathrm{e}^{-\alpha z}), \qquad z\geq 0 \end{aligned} \tag{2}$$

may be adequate in some cases, but not if the Friedel or other oscillations are important features of the true electron density. One does not know in advance how complicated a functional form to use for $\rho(z)$ in the presence of the electrolyte environment.

Our recent calculations [9] have generated one-electron wavefunctions by solving a Schrödinger equation. If $\rho(z)$ is constructed from the $\psi_{\varepsilon,K}$, which in turn are obtained by integrating a differential equation, the shape of $\rho(z)$ will automatically be correctly represented. The equations and our method of solution are presented in Sect. 2. Results are compared with variation for Hg and Ga, two metals of primary interest in electrochemistry.

The representation of the effect of the electrolyte phase is explored in Sect. 3. We are calculating the potential difference $\chi = V(\text{inside}) - V(\text{outside})$ due to the distribution of metal ions and electrons. Since χ is known to be positive [10] and several volts in size, the effect of the electrolyte on χ could be large. Workers on the problem to date [3-5] have represented the electrolyte as a region of dielectric constant greater than unity, a repulsion due to closed-shell species, or both. The dielectric constant corresponds to the electronic polarizability of the electrolyte species. Its effect on the electrons is that of an attractive potential, as the interelectronic repulsion is screened, which extends the electronic tail toward the outside of the metal. The resulting increase in χ is small compared to the decrease in χ due directly to the presence of the dielectric (induced dipoles in direction opposite to the electric field). The effect of the closed-shell repulsion is to push the electronic tail back into the metal, which also decreases χ. Values of several tenths of volts (negative), have been calculated for the change $\delta\chi$, taking enhanced dielectric constant, repulsion, or both into account. This accords with a value for $\delta\chi$ deduced [11] from experimental data with certain assumptions. (Direct measurement of $\delta\chi$, or any quantity involving only the metal part of the interface, is believed to be impossible.)

The potentials used for the electrolyte involve arbitrary choices of parameters, and the repulsion is not carefully justified in terms of the interactions an electron encounters at a layer of water molecules. If the electron does not distort the charge distribution of the water molecules, as energetic considerations suggest, the latter is a source of electrostatic potential. Since the molecule is neutral, its electrostatic potential is zero at infinity and positive everywhere else (attractive interaction for the electron). The exchange and correlation interactions between the metal's conduction electrons and the electrons of the molecule are inherently attractive as well, as they represent a decrease in the electron-electron repulsion. The polarization of the molecular electronic cloud by the conduction electrons may be represented by a "polarization potential" which is also attractive. (Indeed, the dielectric constant region mentioned previously is a crude represent of this.) True molecular potentials are thus wholly attractive.

To justify inclusion of a repulsion, one invokes the arguments of pseudopotential theory [12]. The requirement of orthogonality to electronic wave functions of the electrolyte leads to an increase in kinetic energy for conduction electrons penetrating the electron cloud of electrolyte molecules, and the effect of this increase can be represented by a repulsive pseudopotential. In atomic calculations, the effect of the core electrons on the valence electrons can be treated in this way [13]. In the present case, the repulsive pseudopotential represents the effect of all the electrons of the electrolyte molecules, which are closed-shell species. Energetically, this is analogous to the atomic case. Since the ionization potential of the water molecule is 12.62 eV, and an electron emitted to the vacuum level from bulk water would require additional energy corresponding to the surface potential of water, approximately [14] 0.26 V, the water electrons are 12.9 eV below the vacuum level. The electrons of the metal which overlap the water molecules are those near the top of the conduction band, requiring an energy equal to the work function (4.50 V for Hg, 4.12 V for Ga) to reach the vacuum, so their energies are well above those of the bound electrons of water. For this reason, we can neglect distortion of the electronic distribution of the water molecules, and consider them as a source of potential for the metal electrons.

Application of the above ideas still requires generation and parameterization of a pseudopotential. As attempt to do this is made in Sect. 3. In this section, we also investigate various exchange-correlation potentials, proposed for electron-molecule interactions, calculating their effects using the differential equation method, on the metal electron distribution and on χ. It will be seen that χ is extremely sensitive to the exchange-correlation potential used.

2. Self-consistent field equations

Lang and Kohn [15] developed self-consistent field equations for the electron density at the surface of a solid metal, based on the Hohenberg-Kohn-Sham theorem [16], that the ground state energy (and hence, the wavefunction and all electronic properties) for a system of interacting electrons in an external potential is a functional of the electron density. Let E be the ground state energy of a system of N interacting electrons in some external potential and let $\rho(\vec{r})$ be the corresponding electron density. Lang and Kohn [15] consider a system of N noninteracting electrons that has the same density, $\rho(\vec{r})$, and electronic kinetic energy T_s. They define the exchange-correlation energy as

$$E_{xc} = E - T_s + \int \rho(\vec{r}) v(\vec{r})\, \mathrm{d}\vec{r} - E_C \tag{3}$$

where E_C is the average Coulomb energy of the electron cloud and $v(\vec{r})$ is the external potential. Taking E_{xc} to be a local functional of ρ, one constructs the effective potential

$$v_{\text{eff}} = -v(\vec{r}) + \int \rho(\vec{r}')|\vec{r}-\vec{r}'|^{-1}\,\mathrm{d}\vec{r}' + \delta E_{xc}/\delta\rho \tag{4}$$

and considers the one-electron Schrödinger equation

$$(-\tfrac{1}{2}\nabla^2 + v_{\text{eff}})\psi(\vec{r}) = \varepsilon\psi(\vec{r}). \tag{5}$$

(In this and subsequent equations, we use atomic units, $|e| = \hbar = 1$; the atomic unit of energy is 27.21 eV or 2 Ry.) Thus, from an initial guess for the conduction electron density, the electrostatic potential V_C and the exchange-correlation potential $V_{xc} = \delta E_{xc}/\delta\rho$ is calculated. Then one solves the one-electron Schrödinger equation

$$-\tfrac{1}{2}\nabla^2\psi_{\varepsilon,K} + (V_{xc} - v - V_C)\psi_{\varepsilon,K} = \varepsilon\psi_{\varepsilon,K} \tag{6}$$

with appropriate boundary conditions for all eigenenergies up to the Fermi energy ε_F (K refers to quantum numbers other than ε required to specify the wavefunctions). A new electron density is formed from the eigenfunctions according to (1) and the procedure is repeated until the electron density generated from (6) and (1) is the same as that used to construct V_{xc}.

It does not seem possible to find self-consistent solutions to the equations by direct iteration of the equations (1) and (6). As our procedure is different from that indicated by Lang and Kohn [15], we describe it here. In our application, ρ and the potential depend on z alone. The eigenfunctions are of the form $f(z)\,e^{i\vec{K}\cdot\vec{S}}$, where $\vec{S}$ is a unit vector perpendicular to the z direction and the two-dimensional vectors $\vec{K}$ are chosen to obey periodic boundary conditions, so the degeneracy from the integration over K in (1) is proportional to $\varepsilon_F^2 - \varepsilon^2$. Each eigenfunction, and hence the electron density and potential, is defined by its values at N points z_i, $i = 1, \ldots, N$. We choose M points $\bar{z}_k$ covering the same range of z as the z_i and a reference density ρ_{ref} (sometimes of a simple form like (2), sometimes a density profile from a previous calculation). With each $\bar{z}_k$ is associated a weight W_k from which we generate a Lagrangian interpolation polynomial $w(z)$ which, multiplied by ρ_{ref}, gives an input density $\rho_i(z)$, used to construct $V_C(z_i)$ and $V_{xc}(z_i)$ for $i = 1, \ldots, N$. We fix $\rho(\bar{z}_{M+1})$ equal to ρ_e, the bulk electron density, and assume the electron density equals ρ_e for all $z \leq \bar{z}_{M+1}$. For each input electron density $\rho_i(z_i)$, $i = 1, \ldots, N$, we calculate the position of the ion profile (a step, in the present calculations) required to assure electro-neutrality. This is then used in the calculation of V_C, and also in locating the position of the potential representing the electrolyte environment (see below). Solving the Schrödinger equation (6) by a tabular difference method [17] and using (1) we obtain an output electron density $\rho_0(z_i)$, $i = 1, \ldots, N$, and construct the mean-square relative deviation D where

$$D^2 = \sum_{i=1}^{N} \frac{1}{N}\left[\frac{\rho_i(z_i) - \rho_0(z_i)}{\rho_i(z_i)}\right]^2.$$

The M weights W_k are varied to minimize D, the search for optimum values being carried out by a simplex algorithm [18] in an $(M+1)$-coordinate space. The search is terminated when D gets below 1%. We have verified that our method yields the same density profiles for the cases treated by Lang and Kohn in their original work [15].

There is an important difference between our calculations and those of Lang and Kohn, because we deal with a liquid metal. For a solid metal, the ionic contribution to the potential is clearly not a function of z alone, but it is convenient to first calculate the electron density profile for a one-dimensional ion density profile (jellium), by the theory discussed above, and then obtain the effect of substituting the ionic lattice (using available structural information) by a perturbation procedure [7, 10]. For a liquid metal, there is an average ion density profile instead of a set of ion positions. The average electron density, in principle, ought to be calculated by averaging the electron density for each ionic configuration; our theory assumes it can be obtained from a single calculation using the average ion density profile, a function of z alone. No perturbative insertion of ion positions is involved. For the same reason, the potential includes a pseudopotential for the metal ion cores, averaged over the ion density profile. The potential in the Schrödinger equation being a function of z alone, our problem is truly one-dimensional.

Some information is available about the ion density profile for a liquid metal, experimental [19] and theoretical [20]. Whether it is monotonic or oscillatory is not settled. The present calculations use a step function. Other work [9, 21] investigates the effect of using profiles which are less abrupt or contain oscillations.

We are interested in ascertaining the effect on $\rho(z)$ and the resultant χ of using the full differential equation procedure instead of the variational procedure used [3] formerly. The previous calculations employed the variational functions of Eq. (2) and a two-parameter (but still monotonic) modification.

$$\begin{aligned} \rho &= \rho_e\left(1-\frac{\mathrm{e}^{\alpha z-1+(\alpha/\beta)}}{1+(\alpha/\beta)}\right), & z<x \\ \rho &= \rho_e\frac{\mathrm{e}^{-\beta z-1+(\beta/\alpha)}}{1+(\beta/\alpha)}, & z\geq x \end{aligned} \tag{7}$$

where $x=\alpha^{-1}-\beta^{-1}$. This function is continuous and with continuous derivative at x, and satisfies the normalization condition

$$\int_{-\infty}^{\infty}(\rho-\rho_N)\,\mathrm{d}z=0$$

if ρ_N is a step function at 0 (or a function of type of Eq. (2)). The ion charge density ρ_N is the ion density profile multiplied by the charge per ion (2 for Hg, 3 for Ga). The parameters for the ionic pseudopotentials for the metals are those used previously [3]. Similarly, the electrolyte is modeled in the same way as previously, as a region where the dielectric constant differs from unity and/or a

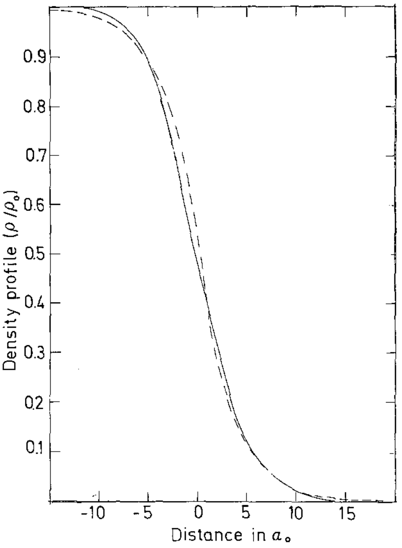

Figure 1. Comparison of self-consistently calculated density profile (*solid line*) with variational density profile (*broken line*) for liquid Ga surface: ρ/ρ_{bulk} plotted against distance from ion (step) profile in a_0

delta-function repulsion. The positions of these potentials depend on the radius of the water molecule and the crystallographic radii of the metal ions.

Fig. 1 shows, for Ga in the absence of electrolyte, electron density profiles as calculated from the Lang-Kohn equations and as obtained variationally. The deviation shows up in calculated values of χ, given by

$$\chi=-4\pi\int_{-\infty}^{\infty}\mathrm{d}z\int_{-\infty}^{z}\mathrm{d}z'\,[\rho_+(z')-\rho(z')] \tag{8}$$

where ρ_+ is the ionic charge distribution. The work function for a metal is computed as $\chi-\mu_e$, where μ_e is the chemical potential of the electrons within the metal.

From the bare Ga surface, we calculate $\chi=9.48$ V from solution of the Lang-Kohn equations, much below the result obtained from variation, 10.51 V. For Hg, the corresponding results are 5.2 V and 5.37 V, quite close. For the higher electron density metal, the variational function is thus less adequate. In calculating the chemical potential of the electrons, we note that the variational and differential-equation calculations differ only in the treatment of the kinetic energy. However, in the latter we calculate the electronic kinetic energy in bulk metal, which is for a uniform electron gas, so we get the Thomas-Fermi expression

$$\frac{\mathrm{d}}{\mathrm{d}\rho_e}\left[\tfrac{3}{10}(3\pi^2)^{2/3}\rho_e^{5/3}\right]=4.785\rho_e^{2/3}$$

as in the variational theory. The calculated work functions for Hg and Ga are 3.38 V and 3.12 V. Trasatti [22] has suggested, from various experimental data, work functions of 4.50 V and 4.25 V for liquid Hg and Ga. Compared to the results of the variational calculations, 3.51 V and 4.25 V, the new values of χ have restored the correct relative values, although both are about 1 V too low. Among other things, a changed ion density profile could change χ values.

The effect of a changed dielectric constant, representing the polarizable electrons of the electrolyte, can be fairly well calculated by assuming the electron density in the presence of the dielectric is essentially that of the bare metal. Then the change in χ, using Eq. (8) and the overall electroneutrality, is

$$\Delta\chi_\varepsilon = -4\pi \int_{-\infty}^{\infty} dz' \left(\frac{1}{\varepsilon(z')} - 1 \right) \int_{z'}^{\infty} dz'' \rho(z'').$$

The dielectric constant $\varepsilon(z)$ differs from unity for $z \geq R_c$, the crystallographic radius of the metal ion. Although a z-dependent ε was used in our previous work, the fall-off of ρ for $z > 0$ means the value of ε just beyond R_c ($\varepsilon = 6$ was used) is most important, and we approximate $\Delta\chi_\varepsilon$ as

$$-4\pi \int_{R_c}^{\infty} dz' (\tfrac{1}{6} - 1) \int_{z'}^{\infty} dz'' \rho(z'') = -\tfrac{5}{6}[V(R_c) - V(\infty)]. \tag{9}$$

Changes in this quantity thus measure changes in the tail of the electron density profile. The Eq. (9) gives −0.27 V and −1.53 V for the variational profiles for Hg and Ga (−0.24 V and −1.01 V from a precise calculation) and −0.32 V and −1.38 V using the profiles from the self-consistent theory. Again, the variational profile is adequate for Hg but not for Ga. (The same is true for the approximation using the bare-surface electron density.) However, errors in $\Delta\chi$ are less than in χ itself.

The same conclusion follows from our calculations on the effect of a repulsive potential

$$V_r = \lambda \delta(z - d_r) \tag{10}$$

representing the effect of the closed-shell cores of the water molecules. We take $\lambda = 0.15$ a.u. or 4.1 eV, and d_r equal to the metal ion radius plus the radius of a water molecule, 0.15 nm or 2.83 a_0. The electron density profile is calculated with V_r added to the external potential, and the value of χ compared with that in the absence of V_r (bare metal). We find decreases in χ of 0.21 V and 0.25 V for Hg and Ga, respectively. Variational calculations gave decreases of 0.13 V and 0.55 V. Here, it is just the distortion in the shape of $\rho(z)$ which is responsible for the change in χ. The variational functions of the form (7) may become quite inadequate for a potential which differs markedly from that of jellium. Since other workers [4] have used a step-function to represent the closed-shell repulsion, we also considered

$$V_r' = \lambda' \theta(z - d_r')$$

with $\lambda' = 0.1$ a.u. and $d_r' = R_c + 0.15$ nm. For Ga, a decrease in χ of 0.24 V was obtained. Finally, we considered the effect of the dielectric constant in the presence of the δ-function barrier by calculating $\Delta\chi_\varepsilon$ according to (9) using the profile obtained in the presence of the barrier. We find −0.23 V for Hg and −1.29 V for

Ga. The barrier pushes the electron density profile back towards the metal, decreasing its values for positive z and hence making $\Delta\chi_\varepsilon$ smaller in magnitude.

Of course none of the barrier calculations are meaningful without a way to choose a value for the parameter λ or λ'. They show only that, with reasonable values for these parameters, the decrease in χ is of a reasonable size. (There is the added satisfaction that our method of solving the self-consistent equations continues to be effective with repulsive potentials present.) The construction of the potential representing the electrolyte is explored in the next section, to ascertain which features are important and to which features results (e.g. χ) are insensitive.

3. Electrolyte potentials

We need to construct the potential due to a layer of water molecules, as seen by a conduction electron of the metal. The distortion of the charge distribution of the water is probably unimportant. The charge distribution and resulting potential of a water molecule is quite complicated [23] in form. Further, different orientations relative to the metal are undoubtedly present in roughly equal proportions [24, 25]. For this reason, we have considered the isoelectronic Ne atom, which of course has a spherically symmetric electron density in the ground state. If the interior of the molecule is most important in the potential, this is a reasonable simplification. If details of the electrostatic potential on the periphery are important, it is not.

Using Clementi's limited-basis Hartree-Fock function [26] for Ne, we calculate the total electron density (depending only on distance from the nucleus) and hence electrostatic potential V_c from Poisson's equation. The exchange-correlation potential V_{xc} in the local approximation is evaluated as $\mathrm{d}(\rho\varepsilon_{xc})/\mathrm{d}\rho$ with the same electron density. Taking ε_{xc} as the sum of the exchange energy density for a uniform electron gas and Wigner's interpolation formula for the correlation energy density [27] we obtain

$$V_{xc} = -\frac{4}{3}\frac{0.458}{r_s} - 0.44\frac{7.8+4r_s/3}{(r_s+7.8)^2} \tag{11}$$

where $4\pi r_s^3\rho/3 = 1$. The resulting V_C and V_{xc} are plotted in Fig. 2. It is noteworthy that the latter is much larger than the former except for r below about 1.8 a_0, the two becoming equal only near 1 a_0. Since centers of the water molecules are distant from the metal ion step functions by 4.95 a_0 for Hg and 4.00 a_0 for Ga, we can anticipate that V_{xc} will be more important than V_C. The atomic potential $V(r) = V_{xc}(r) + V_C(r)$ is converted to the z-dependent potential due to a layer of "water" molecules according to

$$\tilde{V}(z) = \iint \mathrm{d}x\,\mathrm{d}y\,PV(r) = 2\pi P\int_{|z-z_0|}^{\infty} r\,\mathrm{d}r\,V(r) \tag{12}$$

where z_0 is the distance of the water layer from the outermost layer of metal ions and P is the number of water molecules per unit area. Since one water [25, 28] has a cross-sectional area of 9 Å^2 or 30 a_0^2, P is taken as 0.031 a_0^{-2}.

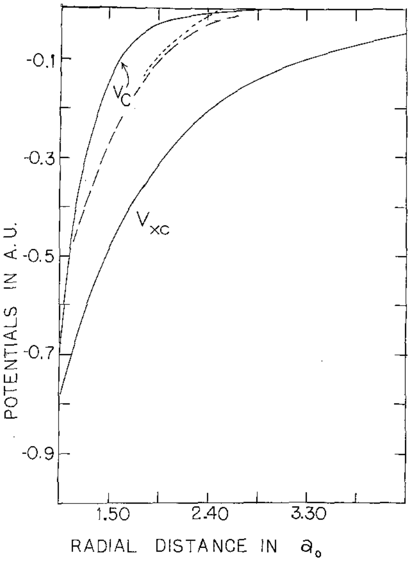

Fig. 2. Coulomb and exchange-correlation potentials for Ne atom (modeling H_2O molecule), in a.u., plotted aginst distance from center, in a_0. *Broken line*: Hara exchange potential. *Dotted line*: Hara potential with Gombás cut-off

A cut-off in $V(r)$ is introduced to represent the repulsive effect of the constraint of orthogonality to the inner shells, i.e. $V(r)=0$ for $r<r_0$. Then

$$\tilde{V}(z)=2\pi P\int_{|z-z_0|}^{\infty} r\,\mathrm{d}r\,V(r), \qquad |z-z_0|>r_0 \tag{13a}$$

$$\tilde{V}(z)=2\pi P\int_{r_0}^{\infty} r\,\mathrm{d}r\,V(r), \qquad |z-z_0|\leq r_0 \tag{13b}$$

where r_0 is determined so that there are no atomic bound states orthogonal to the filled states, i.e. the lowest eigenvalue of the modified potential is zero. With the WKB formula, this means

$$\int_{r_0}^{\infty} \mathrm{d}r(-2V)^{1/2}=\pi/2. \tag{14}$$

We find $r_0=2.338$ and $\chi=9.49$ V for Hg.

The exchange potential (11) needs modification. Slater and Wood [29] and Truhlar [30] give general discussions of exchange potentials. The exchange part of the Kohn-Sham potential (11) approaches $-0.59/r_s$ for low densities ($r_s\to\infty$) whereas the Slater potential [29], $-(3/2)(3\rho/\pi)^{1/3}$, is $-0.916/r_s$. In fact, the potential for the exchange interaction of an electron of momentum k with an electron gas is dependent on the value of k:

$$V_{xc}=-2\left[\frac{1}{2}+\frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right]\left[\frac{3\rho}{\pi}\right]^{1/3} \tag{15}$$

with $\eta=k/k_F$, k_F the Fermi momentum for the gas. The function of η in brackets is 1 for $\eta=0$ and $\frac{1}{2}$ for $\eta=1$; averaging over η produces the Kohn-Sham-Slater potential, appropriate for average exchange for electrons in the atom itself. As discussed at the end of Section 1, the electrons in the tail of the metal conduction band are of higher energy than the valence electrons. Thus, it is reasonable to use the exchange potential for $\eta = 1$, *i.e.* $\frac{2}{3}$ the averaged exchange potential; $-(3\rho/\pi)^{1/3}$ is $-0.61/r_s$, the Wigner exchange. Even more appropriate would be a higher value of η.

The Hara potential [31], used to treat electron scattering by atoms, is Eq. (15) with a recipe for choosing the effective k value. The value of η is now k'/k_F where

$$(k')^2 = k_F^2 + k^2 + 2I.$$

I being the ionization potential of the atom. This takes into account the location of the atomic energy levels relative to the zero of electronic kinetic energy. For our problem, we apply the idea by noting that, since the ionization potential of water is 12.62 eV and the work function of mercury 4.50 V, the effective ionization potential for k' is 8.12 V or 0.298 a.u. For each r k_F is calculated as $(3\pi^2\rho)^{1/3}$, while $k = 0$ because the kinetic energy is included in the work function. Thus

$$\eta^2 = 1 + 0.597(3\pi^2\rho)^{-2/3}$$

gives the value of η to use in V_{xc} (above). In Fig. 2, the Hara potential is shown as a broken curve. We find $r_0 = 0.884$, and $\chi = 7.42$ V. The exchange potential is apparently too strong in the periphery of the atom. Calculations of low-energy electron scattering led workers to the same conclusion [32] and various theories attempted to correct the situation.

Gombás [33] suggested that, for low electron densities, the statistical approach becomes invalid, and argued that the exchange potential should vanish for electron densities less than that corresponding to the boundary density in the Thomas-Fermi-Dirac model, [34] $\rho_0 = 0.0021275\ a_0^{-3}$. Letting $x^3 = \rho_0/\rho$, Gombás writes

$$V_{xc}^{\mu} = -2\left(1 - x + \frac{1-x^2}{2}\ln\left|\frac{1+x}{1-x}\right|\right)\left(\frac{3\rho}{\pi}\right)^{1/3}, \quad x \leq 1 \tag{16}$$

and $V_{xc}^{\mu} = 0$ for $x \geq 1$, thus cutting off the exchange potential. Further, Lindgren and Rosen [32] introduced a correction for self-exchange, a factor of $(1 - 2/Z)^{1/3}$ where Z is the atomic number of the atom. The η-dependent factor of Eq. (15), evaluated at $\eta = 1$, was also put in. Gregory and Fink [32] found that, with the three factors, there was great improvement in electron scattering calculations (although the value of ρ_0 was not crucial), and concluded that the resulting potential represented an "accurate approximation to the actual exchange potential". Using the self-exchange correction and the Gombás cut-off to construct a potential, we found $r_0 = 0.925$. The effect of the Gombás cut-off is shown as a dotted curve in Fig. 2. The self-consistent calculations led to $\chi = 8.40$ V, still unreasonably large.

The above and other calculations show that, when the exchange potential is made less negative, the condition (14) leads to a smaller value of r_0, and a more negative limiting value of V from (13a). The compensation keeps χ large, and $\delta\chi$ large and *positive.* If $\delta\chi$ itself is only several tenths of a volt (negative) as suggested by experiment [11], the effect of the attractive potential must be much less than a volt. The problem is that, according to (13a), $\tilde{V}$ takes a constant negative value for z between $z_0 - r_0$ and $z_0 + r_0$. Note that the WKB criterion (14) does not define $V(r)$ for $r < r_0$; the turning point's being at r_0 for $\varepsilon = 0$ means simply that $V(r)$ is greater than or equal to zero for $r < r_0$. If it is positive, $\tilde{V}$ will be less negative for $z > z_0 - r_0$.

To simulate this, we take $\tilde{V}(z) = 0$ for $|z - z_0| < r_0$, which is 0.925 in the Gombás model. The large r cut-off for the exchange potential is 2.640. The electrostatic potential being small here, we take $V(r) = 0$ for $r > 2.640$; $\tilde{V}(z) = 0$ for $|z - z_0| > 2.640$, and $\tilde{V}(z) = 0$ for $|z - z_0| < 0.925$. Without this last modification, χ is 8.40 V; with it, $\chi = 5.86$ V. Incorporating the Hara modification together with Gombás' cut-off gives $r_0 = 0.8211$, $V(r) = 0$ for $r > 2.668$ and $\chi = 5.74$ V. We conclude that the Gombás cut-off and the proper truncation of $\tilde{V}(z)$ are most important in getting a reasonable potential. Of course, the proper way of obtaining $\tilde{V}(z)$ is by a more complete representation of the atomic pseudopotential $V(r)$, for $r < r_0$. It should also be noted that none of these corrections give the correct behavior of the potential at very large distances, where the exchange-correlation interactions are described by image forces. The role played by this long range behavior within the context of the present problem thus remains a challenge for future study.

4. Discussion

Simple reasonable calculations establish that the components of the metal play an important role in the polarizable electrochemical interface, although their contribution is usually ignored in elaborating models for, e.g., electrical properties. Reliable quantitative calculations of the metal contribution are more difficult to achieve. We have tried to indicate the problems that arise and how some of them may be dealt with. The property considered here is χ; its variation with electrode charge is a contribution to the measurable interfacial capacitance.

We have a procedure for generating the distribution of the conduction electrons at a liquid metal surface, given the profile of the ions and the ion-electron interaction. We have used a step function ion profile here, but the calculations can be performed [21] given any profile, and it is likely that new theories for the ionic interactions at a metal surface [35] will be generating such profiles. Similarly, a better representation for the ion-electron interaction may be developed.

For a reliable calculation of χ in the presence of the electrolyte phase, the potential $\tilde{V}(z)$ must be given accurately. If no way of obtaining $\tilde{V}(z)$ directly is available, it must be generated by superposition of single-molecule potentials, $V(r)$ [36]. One parameter whose effect we have not investigated is the distance z_0, the position of the first layer of electrolyte molecules from the metal. Its variation with charge can have a major effect [37] on capacitance. The value of z_0 should be determined by a calculation (minimization of metal-electrolyte interaction energy, as is done for chemisorbed layers [38]) rather than chosen as done here. Finding $V(r)$ if the electrolyte phase is an aqueous solution could involve use of molecular electron density distributions [23, 26] from which electrostatic and exchange-correlation potentials could be computed. These would be rather complicated in form, and would have to be averaged over molecular orientations with respect to the interface. It may be that the electrostatic potential could be represented by the potential of a simple multiple moment [23]. Variational calculations for the conduction electrons, using such a representation of the solvent molecules, have been performed [37] for the effect of the solvent on the metal contribution to the capacitance.

As for the exchange-correlation potential, it may be possible to generate it from the electron density of an isoelectronic species, as the calculations of Sect. 3 indicate that the most important effects come from the electron density 1-2 a_0 from the center. The last form used was the Slater-Kohn-Sham potential (15) with the Hara (effective k) and Gombás (Eq. (16)) corrections. As shown in Fig. 2 (broken curve ≡ Hara potential, dotted line ≡ with Gombás cut-off), the exchange-correlation potential remains more important than the electrostatic potential in the range of distance from 1 to 2 a_0. The representation of the effect of orthogonality of metal electrons to those of the electrolyte molecules (closed-shell repulsion) is crucial when $\tilde{V}(z)$ is generated from the atomic $V(r)$. It is not sufficient to set $V(r) = 0$ for $r < r_0$ (pseudopotential of Ashcroft type).

A great amount of experimentation is needed. To save time, many of these calculations could be done variationally, to determine gross features and orders of magnitude. Variational functions more complex than Eq. (2) have recently been introduced for this problem [39]. As the work of Sect. 2 shows, however, quantitative results require the self-consistent Lang-Kohn calculations.

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