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## Self-consistent calculation of the electron distribution at a jellium surface in a strong static electric field

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The Hohenberg-Kohn-Sham formalism in local-density approximation is used to calculate selfconsistently the effective potential and electron density profile at the surface of a jellium slab in a strong static electric field. In the wide range of induced surface-charge densities accessible to experiments in electrolytic cells, the shape of the calculated electron density profiles is characterized by suitable moments, and the induced charge density by its center of mass and by its width, which are related to static and to optical response properties, respectively. Comparison with previous work reveals the importance of selfconsistency.

The distribution of electrons at a metal surface in a strong static electric field is a topic of current interest for the interpretation of many experiments on metal/electrolyte interfaces. The metal contribution to the differential capacity of the interface, related to the center of mass  $z_0(\sigma)$  of the induced surface-charge density  $\sigma$ , has recently been discussed on the basis of density-functional variational calculations using an ansatz for the electron density n(z) within a jellium-type model of the metal.<sup>1,2</sup> The spread  $\lambda(\sigma)$  of the induced static charges, on the other hand, is important for optical properties, and has recently been discussed in connection with ellipsometry measurements on a positively charged gold surface.<sup>3,4</sup>

Information about mean position  $z_0(\sigma)$  and width  $\lambda(\sigma)$ of the induced charged-density profile is not easily obtained from such experiments. The metal contribution to the differential capacity of an electrolytic cell is hard to isolate,<sup>2</sup> and the evaluation of  $\lambda(\sigma)$  from ellipsometry data depends drastically on the optical theory employed. Whereas classical optics indicates a linear relationship,<sup>3</sup>  $\lambda = \text{const} \times \sigma$ , a more ambitious calculation<sup>4</sup> based on a nonlocal optical theory deduces from the same data a value  $\lambda \approx 2.5-3$  Å, nearly independent of  $\sigma$ .

Theoretical knowledge about the structure of the charged metal surfaces is also very limited, even within the jellium model, which will be considered exclusively in the following. For small surface-charge density ( $\sigma \sim 10^{-3}e/\text{Å}^2$ ), Lang and Kohn<sup>5</sup> calculated the induced charge density and its center of mass  $z_0$  within the local-density approximation<sup>6</sup> of the Hohenberg-Kohn-Sham formalism.<sup>7</sup> These exact results describe the linear response to a weak external electric field, but cannot appropriately account for the effect of electric fields of the order of 1 V/Å occurring at metal/electrolyte interfaces. A quantum-mechanical response calculation for strong external electric field has been performed by Theophilou and Modinos.<sup>8</sup> This calculation is not reliable, however, since it is based on an inconsistent approximation scheme.<sup>9</sup>

Variational calculations with a restricted ansatz for the electron density have also been performed for a wide range of external electric field strengths,<sup>1,2</sup> and the results are consistent<sup>1</sup> with those of Lang and Kohn.<sup>5</sup> However, the range of validity of these calculations is hard to estimate. A quantum-mechanical calculation for a negatively charged

metal surface becomes, for instance, meaningless if the maximum of the effective potential becomes smaller than the Fermi energy, so that the electrons would leak out. This physical restriction is apparently not included in the variational calculations which make the ansatz that the electron density decays exponentially outside the metal.<sup>1,2</sup>

In view of this situation we have extended the selfconsistent approach of Lang and Kohn to jellium surfaces in strong electric fields. A detailed discussion of our calculation procedure and results covering the whole range of metallic densities will be given elsewhere. In the present Rapid Communication we consider only one electron density corresponding to a Wigner-Seitz radius  $r_s = 3$ , which allows comparison with previous theoretical work<sup>1,8</sup> and with experiments on gold.<sup>3</sup>

For convenience, we consider a slab geometry perpendicular to the z direction, with a jellium slab of constant density  $n_+ = 5.97 \times 10^{22}$  cm<sup>-3</sup> located at 0 < z < 2b. To simulate the effect of an electrolyte which prevents electrons from tunneling away from a negatively charged metal surface, we introduce infinite potential barriers symmetrically with respect to the slab at z = -a and z = 2b + a. Electron density n(z) and effective potential  $v_{eff}(z)$  are assumed to be symmetric with respect to z = b. A suitable choice of parameters is b = 8 Å and a = 4.8 Å, implying that near the infinite barrier, n(z) is exponentially small and  $v_{eff}(z)$  is larger than the Fermi energy in the interesting range of surface-charge densities:

Here

$$\rho(z) = -e[n(z) - n_{+}\theta(z)\theta(2b - z)]$$

 $\sigma = \int_{a}^{b} dz \ \rho(z) = \int_{a}^{b} dz \ \delta \rho(z) \ .$ 

is the total charge density and  $\delta\rho(z)$  the induced charge density. The equations to be solved self-consistently are<sup>6</sup>

$$n(z) = \frac{m}{\pi \hbar^2} \sum_{\epsilon_{\nu} < \epsilon_F} (\epsilon_F - \epsilon_{\nu}) |\psi_{\nu}(z)|^2 , \qquad (2)$$

and Schrödinger's equation

$$-\frac{\hbar^2}{2m}\psi_{\nu}^{\prime\prime}(z) + (v_{\rm eff}[n;z] - \epsilon_{\nu})\psi_{\nu}(z) = 0 \quad , \tag{3}$$

where  $\epsilon_{\nu}$  and  $\psi_{\nu}$  are, respectively, the energy eigenvalue and

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<u>31</u> 6843

$$v_{\rm eff}[n;z] = \phi(z) + \mu_{\rm xc}[n(z)] \quad , \tag{4}$$

with<sup>6</sup>

$$\mu_{\rm xc}(n) = -\frac{e^2}{a_0} \frac{d}{dn} \left[ n \left( \frac{0.458}{r_s(n)} + \frac{0.44}{r_s(n) + 7.8} \right) \right] , \qquad (5)$$

where  $a_0 = 0.529$  Å is Bohr's radius and

$$r_s(n) = \left(\frac{1}{3}4\pi na_0^3\right)^{-1/3} . \tag{6}$$

The electrostatic energy  $\phi(z)$  is obtained from Poisson's equation and can be written as

$$\phi(z) = \phi(b) + 4\pi e$$

$$\times \left[ D(\sigma) - z \sigma + \int_{-a}^{z} dz'(z - z')\rho(z') \right] , \qquad (7)$$

where

$$D(\sigma) = \int_{-a}^{b} dz \, z \, \rho(z) = D(0) + \sigma z_0(\sigma) \tag{8}$$

is the electric dipole moment (per unit area) of the charged surface, and

$$z_0(\sigma) = \frac{1}{\sigma} \int_{-a}^{b} dz \, z \, \delta\rho(z) \tag{9}$$

is the center of mass of the induced charge density. According to Eqs. (1) and (2), the Fermi energy of the slab is determined from

$$\frac{m}{2\pi\hbar^2} \sum_{\epsilon_{\nu} < \epsilon_{F}} (\epsilon_{F} - \epsilon_{\nu}) = bn_{+} - \frac{\sigma}{e} \quad . \tag{10}$$

We solved the self-consistent problem iteratively  $(v^{(\nu)} \rightarrow n^{(\nu)} \rightarrow v^{(\nu+1)})$  but, since direct iteration does not converge, we employed a suitable modification of Newton's method, similar to that described by Lang and Kohn.<sup>6</sup> After 5-8 iteration steps a sufficient accuracy was obtained.

Figure 1 shows electron density profiles for several values of the surface-charge density  $\sigma$ . For the neutral surface our results for electron density and effective potential are in full numerical agreement with the results of Lang and Kohn.<sup>6</sup>



FIG. 1. Self-consistent electron density profiles for a neutral surface and three different surface-charge densities  $\sigma$  given in units of  $10^{-3}e/\text{Å}^2$ . The system parameters are given in the text. The full line sketches the jellium, the broken lines mark a shift by  $s = \sigma/(en_+)$ .

This shows that neither the finite thickness of the metal slab nor the infinite barrier has an effect on the electron density profile in the surface region.

As a function of  $\sigma$ , the shape of the calculated density profiles changes considerably. For small values of  $\sigma$  the induced charge density is located in the low-density tail of the profile. For negative values of  $\sigma$ , the density in the tail is increased; the surface is more diffuse than in the neutral case. For positive  $\sigma$ , electrons are removed from the tail and the profile becomes steeper. This behavior follows already from linear response arguments. With furtherincreasing positive values of  $\sigma$ , a displacement of the profile into the jellium becomes apparent.

Figure 2 shows our results for the center of mass  $z_0$  (crosses) and the full width at half maximum  $\lambda$  (asterisks) of the induced charge-density profile as a function of  $\sigma$ . With increasing  $\sigma$ , the location  $z_0$  of the induced charge density shifts from the low-density tail (negative values of  $z_0$ ) towards the jellium. Its width  $\lambda$  shrinks a little as it approaches the region of higher electron density.

The range of  $\sigma$  values shown in Fig. 2 is, according to Chao and Costa,<sup>3</sup> accessible to experiment. Since the width  $\lambda$  of the induced charge density can be considered as the screening length of the static electric field, we see from Fig. 2 that for  $\sigma = 0.06e/\text{Å}^2$ , corresponding to an external electric field of 10.8 V/Å, the field would penetrate about  $z_0 + \frac{1}{2}\lambda \approx 1.2$  Å into the jellium. One would expect that a real metal surface exposed to such giant electric fields would emit ions.

For the jellium model, on the other hand, arbitrary positive values of  $\sigma$  are possible (at least for a half-space geometry). It is instructive to consider the asymptotic limit  $\sigma \rightarrow \infty$  for a jellium half-space. Since deformation of the density profile toward steeper profiles should saturate, ow-



FIG. 2. Center of mass  $-z_0$  (+) and width  $\lambda$  (\*) of the induced charge density as a function of  $\sigma$ . The broken line gives the asymptotic behavior of  $z_0$  corresponding to a rigid shift of the density profile. Also shown are  $z_0$  results of Ref. 8 (curve a) and Ref. 1 (curve b).

ing to Fermi pressure effects, asymptotically a rigid displacement remains, which makes the discussion trivial. A rigid displacement s of the electron density profile of a neutral surface produces a surface-charge density  $\sigma = en_+s$ , with center of mass  $z_0(\sigma) = \frac{1}{2}s = \sigma/(2en_+)$ , indicated by the broken straight line in Fig. 2. The width  $\lambda$  of the induced charge-density profile increases monotonically with increasing displacement s, and asymptotically approaches the value of s.

Although the asymptotic  $(\sigma \rightarrow \infty)$  behavior is not yet reached for the  $\sigma$  values shown in Fig. 2, our numerical results are consistent with this trivial limit. Curve a, on the other hand, showing that the result of Theophilou and Modinos<sup>8</sup> which compares most favorably with ours, is neither consistent with this large- $\sigma$  limit nor with the linear response limit.

The  $(r_s = 3)$  result of Schmickler and Henderson<sup>1</sup> is also shown in Fig. 2 (curve b). For small values of  $\sigma$ , it is in excellent agreement with our calculation. For large negative values of  $\sigma$ , large discrepancies occur, since our calculations include, and are limited by, the physical effect that electrons eventually leak out of the metal. For large positive values of  $\sigma$ , the variational results<sup>1</sup> seem also to deviate systematically from our exact results. The reason may be that it is not sufficient to consider only low-order gradient terms in the variation functional of the electron density,<sup>1</sup> if the correct density profile becomes very steep.

The shape of the electron density profile on the vacuum side is characterized by the moments

$$l^{(\nu)} = \frac{1}{n_{+}} \int_{-a}^{s} dz \, (s-z)^{\nu} n(z) \quad , \tag{11}$$

where  $s = \sigma/(en_+)$ . For the sake of simplicity, we consider only the zeroth and first moment, determining the number (per unit area) of spilled-out electrons,  $n_+l^{(0)}$ , and their center of mass (with respect to the plane z = s)

$$d = l^{(1)}/l^{(0)} {.} (12)$$

Figure 3 shows a correlation plot of d vs  $l^{(0)}$ . For the half-space geometry without infinite barrier, density profiles of the form n((z-s)/R) appear in this plot on the same straight line through the origin. The position on this line then depends only on R, not on s. The commonly used<sup>2</sup> exponential model

$$n(z) = \frac{1}{2}n_{+} \times \begin{cases} \exp[(z-s)/R], & \text{if } z \le s, \\ 2 - \exp[-(z-s)/R], & \text{if } z > s, \end{cases}$$
(13)

- <sup>1</sup>W. Schmickler and D. Henderson, Phys. Rev. B 30, 3081 (1984).
  <sup>2</sup>V. I. Feldman, A. A. Kornyshev, and M. B. Partenskii, Solid State Commun. 53, 157 (1985).
- <sup>3</sup>F. Chao and M. Costa, Surf. Sci. 135, 497 (1983).
- <sup>4</sup>K. Kempa, Surf. Sci. (to be published).
- <sup>5</sup>N. D. Lang and W. Kohn, Phys. Rev. B **3**, 1215 (1971); **7**, 3541 (1973).
- <sup>6</sup>N. D. Lang and W. Kohn, Phys. Rev. B 1, 4555 (1970).



FIG. 3. Correlation plot of diffuseness parameters d and  $l^{(0)}$  for the given values of  $\sigma$ . The straight line indicates the correlation for the exponential model, Eq. (13).

leads, for instance, to the straight line with slope  $d/l^{(0)} = 2$ indicated in the figure. The points in Fig. 3 apparently converge for large values of  $\sigma$ , which indicates again that the change of the density profile with increasing  $\sigma$  finally reduces to a rigid displacement. For negative values of  $\sigma$ , the extension of the low-density tails is larger, and the surface becomes more diffuse than for the exponential profile.

From Fig. 3 we conclude that the electron density in the vacuum region is remarkably well described by the exponential ansatz, especially for positive surface charges. For reliable results on the surface structure in the large range of surface-charge densities  $\sigma$ , which is accessible to experiments in electrolytic cells, fully self-consistent quantum-mechanical calculations turned out to be indispensable. Further details and the discussion of other  $r_s$  values are left to a future publication.

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<sup>7</sup>P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964);
 W. Kohn and L. J. Sham, *ibid.* 140, A1133 (1965).

<sup>8</sup>A. K. Theophilou and A. Modinos, Phys. Rev. B 6, 801 (1972).

<sup>9</sup>The neutral surface is described by a non-self-consistent *ad hoc* model for the effective potential; the changes of electron density and effective potential induced by an external electric field are calculated self-consistently. Different model potentials lead to completely different results.

6845