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Static electronic perturbations of metallic surfaces

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We present a theory of charge distributions induced at a jellium surface by a static applied potential. Exact expressions are derived for the changes in surface potential, and the total potential barrier in terms of the unperturbed electron distribution and the change in the latter due to adding electrons to the jellium. These results are applied to a simple chemisorption model and the induced dipole moment is calculated as a function of proton position for several r_s values.

I. INTRODUCTION

In this paper we examine the effect of a static external perturbation on the electron distribution near a metallic surface. Problems of this sort arise, for example, in field emission or chemisorption, where one requires knowledge of the perturbation of the surface region caused by an applied uniform field or an external localized charge. While quite a few approximate treatments of this problem have been presented,[1] we report here several exact results in this area. We note that exact results have already been presented for the unperturbed jellium surface.[2,3]

We shall first consider linear-response theory, and seek the induced charge density due to a weak point charge. The positive background is taken to be a jellium of charge density ρe, whose surfaces are at $z = 0$ and $z = -L$ (Fig. 1). The induced charge density at point $\vec{r}$ due to a point charge at $\vec{r}\,'$ is denoted by $-en_i(z, z', x-x', y-y')$ because of translational invariance parallel to the surface. In order to calculate the average value of some function $f(z)$ over n_i we do not require the full n_i since

$$\int f(z) n_i \, d^3r = \int f(z)\, dz \int \int n_i(z, z', x-x', y-y') \times d(x-x') d(y-y') . \tag{1}$$

The integral of n_i over x', y' represents the response at z due to a uniform superposition of charges over a plane at z'. Therefore, within the framework of linear-response theory, the response function for a plane of charge is sufficient for determining the average of any $f(z)$ for an *arbitrary* applied charge distribution. We need therefore only consider $n_i(z|z')$ the induced density at z due to a charge plane at z'.

It will be convenient to distinguish between $n_i(z|z')$ and $n(z|z')$. The latter represents the same response function as $n_i(z|z')$ except that it corresponds to a *neutral* system. Electrons are added to or removed from the system, by grounding for example, in order to compensate for the extra charge of the applied plane (Fig. 1).

II. HALF-MOMENT

We now derive an expression for the change in potential difference between the jellium surface

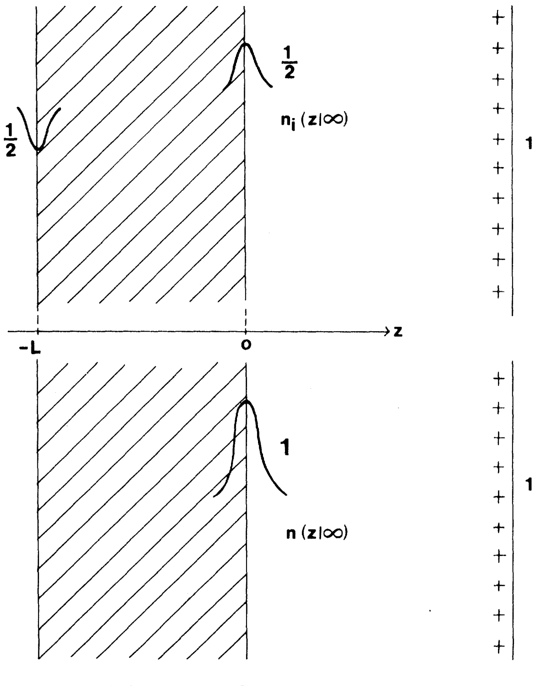

FIG. 1. Solid curves schematically represent induced electron distribution for distant applied charge plane of unit surface charge density. Upper curve corresponds to isolated jellium, while lower curve corresponds to grounded jellium. Numbers indicate total number of electrons per unit area, associated with each distribution.

and bulk due to an external charge plane at z. The jellium is taken to be grounded, so that the overall system is neutral. Momentum conservation, as applied to the total system, requires that the force acting on the external charge plane be equal and opposite to that acting on the jellium background.

Calculating these forces directly from the Feynman-Hellman theorem,[4] we obtain

$$\sigma e E_0(z) = -\rho e \int_{-L}^{0} dz' \bar{E}(z'|z) , \tag{2}$$

where E_0 is the unperturbed electric field, $\bar{E}(z'|z)$ is the total change in the electric field due to the applied charge plane at z, and σe is its surface charge density. The left-hand side of this equation gives the force per unit area acting on the applied charge plane, and the right-hand side that acting on the jellium background. Without any loss in generality in the linear response theory we take $\sigma = \int dz' n(z'|z) = 1$.

For an applied charge plane near the $z = 0$ surface we may take $L = \infty$ since for the neutral system the field $\bar{E}$ goes to zero rapidly in the bulk. The integral appearing in Eq. (2) then gives the change in potential difference between the surface and the bulk in terms of the unperturbed field E_0.

Equation (2) is readily related to the induced electron distribution $n(z'|z)$. Integrating it by parts we obtain

$$E_0(z) = \rho \int_{-\infty}^{0} dz' \, z' \frac{\partial}{\partial z'} \bar{E}(z'|z) . \tag{3}$$

$\bar{E}(z'|z)$ is related to the change in the charge distribution by Poisson's equation

$$\frac{\partial \bar{E}(z'|z)}{\partial z'} = 4\pi e[\delta(z'-z) - n(z'|z)] . \tag{4}$$

Inserting Eq. (4) into Eq. (3) yields

$$E_0(z) = 4\pi\rho e \left(z\Theta(-z) - \int_{-\infty}^{0} dz' \, z' n(z'|z) \right) , \tag{5}$$

where $\Theta(z)$ is the Heaviside step function. The specific moment of n which appears in this equation shall be referred to as the half-moment.

For large negative z the applied charge plane is in the bulk where the unperturbed field E_0 is zero. In this case we can see from Eq. (5) that the half-moment is equal to z, i.e., it coincides with the plane position. As z approaches the surface the difference between the half-moment and the plane position varies as $E_0(z)$. On the vacuum side of the surface the half-moment approaches zero monotonically as does $E_0(z)$.

This shows that the change in the potential difference between the jellium surface and bulk is exactly zero for a weak applied electric field (charge plane at infinity) and furthermore implies that $n(z|\infty)$ oscillates about zero within the solid, since the half moment is zero. This is rather surprising at high densities since the unperturbed electron density is rather smooth in this case. This is however indeed confirmed by explicit numerical calculations.[5]

Differentiating Eq. (5) with respect to z we obtain

$$\frac{\partial E_0}{\partial z} = 4\pi\rho e \left(\Theta(-z) - \frac{d}{dz} \int_{-\infty}^{0} dz' \, z' n(z'|z) \right) . \tag{6}$$

The unperturbed field E_0 is related to $n_0(z)$, the unperturbed electron density, by Poisson's equation

$$\frac{\partial E_0}{\partial z} = 4\pi e[\rho\Theta(-z) - n_0(z)] . \tag{7}$$

Inserting Eq. (7) into Eq. (6), we obtain

$$\frac{d}{dz} \int_{-\infty}^{0} dz' \, z' n(z'|z) = n_0(z)/\rho . \tag{8}$$

Since $n_0(z)$ is positive for all z, we see that the half-moment increases *monotonically* from large negative values in the bulk to zero as z approaches infinity.

III. FULL MOMENT

We now go on to consider the *full* moment of the induced electron distribution, which is directly related to the change in the total potential barrier. The electron density response of the *isolated* jellium to an external plane of charge at position z_1 is given by

$$n_i(z|z_1) = \int dz' K(z|z') \phi_a(z'|z_1) , \tag{9}$$

where $K(z|z') = K(z'|z)$ (Ref. 6) is the usual linear response kernel, and ϕ_a is the applied potential

$$\phi_a(z|z_1) = -2\pi e |z - z_1| , \quad \sigma \equiv 1 ; \tag{10}$$

an arbitrary constant may be added to ϕ_a, corresponding to fixing the zero of potential, and has no effect on the induced electron density. In order to generate information about the vacuum side we shall use the symmetry property $K(z|z') = K(z'|z)$.

Consider now the density response to a charge plane at z_1 and an oppositely charge plane at $z_2 > z_1$

$$n(z|z_1) - n(z|z_2) = \int dz' K(z|z') [\phi_a(z'|z_1) - \phi_a(z'|z_2)] . \tag{11}$$

We note that the n in the left-hand side of this equation can be replaced by the n_i since the total applied charge is zero in this case.

Taking the full z moment of Eq. (11) and using the symmetry of $K(z|z')$, we obtain

$$\int_{-\infty}^{\infty} dz\, z[n(z|z_1) - n(z|z_2)] = \int_{-\infty}^{\infty} dz'[\phi_a(z'|z_1) - \phi_a(z'|z_2)] \times \int_{-\infty}^{\infty} dz\, zK(z'|z) . \tag{12}$$

The last integral in Eq. (12) is simply proportional to $n_i(z|\infty)$, the response of the isolated jellium to a charge plane at infinity:

$$2\pi e \int_{-\infty}^{\infty} dz\, zK(z'|z) \equiv n_i(z'|\infty) . \tag{13}$$

Inserting this relation, as well as the applied potentials [Eq. (10)], in Eq. (12) we obtain

$$\int_{-\infty}^{\infty} dz\, z[n(z|z_1) - n(z|z_2)] = -2\left(z_1 \int_{-\infty}^{z_1} dz' n_i(z'|\infty) + \int_{z_1}^{z_2} dz'\, z' n_i(z'|\infty) - z_2 \int_{-\infty}^{z_2} dz' n_i(z'|\infty)\right) \tag{14}$$

The last term vanishes as z_2 tends to infinity since the total induced charge for the isolated system is zero, and the last integral in Eq. (14) approaches zero exponentially. In this limit, Eq. (14) becomes

$$\begin{aligned}\int_{-\infty}^{\infty} z\, dz[n(z|z_1) - n(z|\infty)] &= -2\left(z_1 \int_{-\infty}^{z_1} dz' n_i(z'|\infty) + \int_{z_1}^{\infty} z' n_i(z'|\infty) dz'\right) \\ &= 2\left(z_1 \int_{z_1}^{\infty} dz'\, n_i(z'|\infty) - \int_{z'}^{\infty} z' n_i(z'|\infty) dz'\right)\end{aligned} \tag{15}$$

where the last line follows from the fact that the total induced charge is zero for the isolated system.

For z_1 "near" the $z = 0$ jellium surface, i.e., sufficiently to the right of the $z = -L$ surface such that the induced charge distribution localized near the latter is negligible at z_1, we can replace $2n_i(z|\infty)$ by $n(z|\infty)$ (see Fig. 1). Equation (15) then becomes

$$\int_{-\infty}^{\infty} dz'\, z' n(z'|z) = \int_{0}^{z} dz' z' n(z'|\infty) + z \int_{z}^{\infty} dz' n(z'|\infty) , \tag{16}$$

where we have used our previous result, Eq. (5), that the half-moment is zero for $z = \infty$.

This relation expresses the induced moment for any plane position in terms of the universal function $n(z|\infty)$ which represents the charge induced by a plane at infinity, or equivalently the change in electron distribution due to adding electrons to the neutral jellium.[7]

The qualitative features of the full moment are readily seen from Eq. (16). For large negative z the plane is in the bulk and the induced moment coincides with the plane position. This follows from Eq. (16) since the first integral approaches zero by Eq. (5) while the second approaches unity. The full moment increases to zero at $z = 0$ as it should since $n(z|0) = -dn_0/\rho dz$ corresponding to an infinitesimal displacement of the unperturbed electron distribution n_0. The moment then approaches a constant value as z approaches infinity.

IV. WORK FUNCTION

We now use Eq. (16) to derive a relation between the work function W and $n(z|\infty)$. It follows from Poisson's equation, that the change in the total electrostatic potential barrier Φ_B due to an applied charge plane at z and a compensating number of electrons is given by

$$\delta\Phi_B = 4\pi e \int_{-\infty}^{z} (z - z') n(z'|\infty) dz' , \tag{17}$$

where Eq. (16) has been used as well as the fact that the half-moment is zero.

If we apply a continuum of such planes, each of infinitesimal surface charge, between $z = 0$ and $z = -D$, we arrive at the configuration shown in Fig. 2. For D a macroscopic distance, we have a jellium of density $\rho + \delta\rho$ with free surface at $z = 0$, in contact with a jellium of density ρ at $z = -D$. The total $\delta\Phi$ corresponding to this situation is simply calculated by integrating Eq. (17) over the applied plane positions, i.e., $z = 0$ to

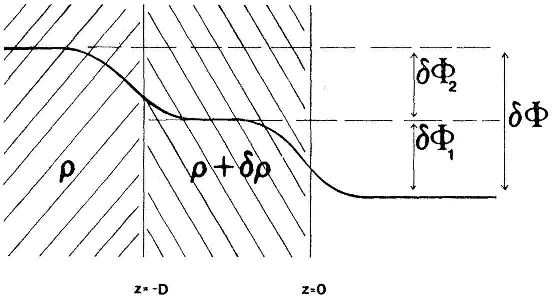

FIG. 2. Schematic representation of jellium modified by uniformly increasing density of macroscopic portion of jellium. The total potential barrier change is resolved into two components, one at the interface of the two slightly different jelliums and the other at the free surface.

$z = -D$.

$\delta\Phi$ is composed of two parts, that at the free surface, $\delta\Phi_1$, and that at $z=-D$, $\delta\Phi_2$. The latter is however known since the electrochemical potential is constant[8] in space; therefore,

$$e\delta\Phi_2 = \mu(\rho+\delta\rho) - \mu(\rho) = \delta\rho\,\frac{d\mu(\rho)}{\delta\rho}\,, \tag{18}$$

where μ is the bulk chemical potential.

Since the change in work function is given by

$$\delta W = \delta(-e\Phi_1 - \mu) = -e\delta\Phi_1 - \delta\rho\,\frac{d\mu}{d\rho}$$
$$= -e(\delta\Phi_1 + \delta\Phi_2) = -e\delta\Phi\,, \tag{19}$$

integration of Eq. (17) yields

$$\frac{\delta W}{\delta\rho} = 4\pi e^2 \int_{-\infty}^{0} dz\, z \int_{-\infty}^{z} n(z'|\infty)\,dz'\,, \tag{20}$$

where we have integrated by parts and have set $D=\infty$. Further partial integration is not possible since $z^2 n(z|\infty)$ does not vanish at minus infinity because of the Friedel oscillations.

V. NONLINEAR THEORY

Up until now we have only considered linear response theory. In Eq. (2), for example, the field acting on the applied charge plane was taken to be $E_0(z)$, the unperturbed field. In the exact theory the latter is replaced by the *total* electric field acting on the applied charge plane, i.e., one must add to $E_0(z)$ the unknown field $E_s(z)$:

$$\sigma e[E_0(z) + E_s(z)] = -\rho e \int_{-\infty}^{0} \bar{E}(z'|z)\,dz'\,. \tag{21}$$

This induced or screening field is in fact the dominant term at large distances since the unperturbed field $E_0(z)$ is of very short range.

In the limit of an infinitely distant applied plane however we know the total field acting on the plane, it is simply $-2\pi\sigma e$, where σe is the applied plane's surface charge density. The analog of Eq. (5) is therefore the exact relation

$$\frac{\sigma^2}{2} = \frac{1}{2}\left(\int_{-\infty}^{\infty} dz\, n(z|\infty)\right)^2 = \rho\int_{-\infty}^{0} dz\, z n(z|\infty)\,. \tag{22}$$

The left-hand side of Eq. (22) is obviously zero in linear-response theory, thus reducing to our previous result. The half-moment is therefore exactly quadratic in the applied surface density and varies inversely as the jellium density.

VI. NUMERICAL APPLICATION CHEMISORPTION

We have compared all of the analytical results presented above with detailed numerical calculations carried out by Lang[10] and have found excellent agreement between the two for both our linear-response results as well as our nonlinear result equation (22).

As a numerical application of the above results we consider the induced dipole moment due to an external point charge. The induced dipole moment is proportional to the change in potential, which is given by Eq. (17) in linear-response theory. This therefore provides a simple model for the induced-dipole moment in chemisorption.

We used the $n(z|\infty)$ computed by Lang and Kohn[5] to calculate the induced-dipole moment as a function of the distance of the proton from the jellium surface. The results are shown in Fig. 3, for r_s values 1.5, 2, 4, and 5. The dipole moment is zero for the proton at the jellium surface, and increases slowly as the proton moves into the vacuum. For very large distances on the vacuum side, the dipole moment increases linearly with distance, as is obvious from Eq. (17). Although not visible in Fig. 3 the dipole moment oscillates about zero as the proton penetrates into the jellium. This is scarcely visible for the $r_s = 1.5$ curve while it is only further into the jellium that the higher r_s curves show these oscillations.

We note that the induced dipole moment is positive for proton positions in the vacuum, which corresponds to a reduction of the work function. These results are quite different from those[9] obtained in simplified calculations based on a gradient expansion of the electron kinetic energy.

There one obtains negative induced dipole moments up to distances of approximately 1.3 a.u., and the size of the induced moments are approximately one order of magnitude smaller than those obtained here using the more accurate charge distributions obtained by Lang and Kohn.[5] Here again

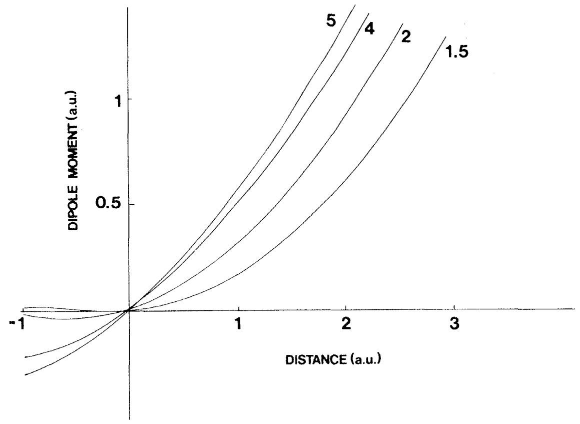

FIG. 3. Induced-dipole moment as a function of proton distance from the jellium surface. The curves correspond to $r_s = 1.5$, 2, 4, and 5.

excellent agreement is obtained with Lang's[10] results for the induced-dipole moment.

We do not claim that linear response theory provides an adequate description of chemisorption but we emphasize that when applied self-consistently to the chemisorption problem, it yields quite different results from those obtained in theories where the gradient expansion approximation is used.

VII. CONCLUSION

In the summary we have presented the following exact results within the framework of linear response theory: (i) The half-moment of the induced charge distribution is given in terms of the unperturbed electric field [Eq. (5)]; (ii) the full moment of the induced charge distribution is given in terms of the universal function $n(z|\infty)$ [Eq. (17)].

Within linear-response theory these results are applicable to an arbitrary applied potential, as discussed in Sec. I.

In addition the density derivative of the work function is given in terms of $n(z|\infty)$ [Eq. (20)]. Finally, Eq. (22) gives the exact half-moment for an applied external field, including nonlinear effects. We note however that in deriving this latter nonlinear result, it was assumed that the jellium is not "ionized" by the applied field. All these results are in excellent agreement with detailed numerical calculations carried out by Lang.[10]

We have also presented a linear-response theory of the induced-dipole moment in chemisorption. The induced-dipole moment has been calculated, as a function of proton position for several r_s values. For proton positions in the vacuum, the linear theory predicts a positive dipole moment, corresponding to a decrease in the work function.

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[6] D. Des Cloizeaux, in *Theory of Condensed Matter* (International Atomic Energy Agency, Vienna, 1969), p. 325.

[7] It is also possible to derive this result from N. D. Lang and W. Kohn's work [Phys. Rev. B 3, 1215 (1971); 8, 6010 (1973)] together with our result that the half-moment is zero for an applied electric field. To do so, however, requires that one only consider perturbations for which the bulk chemical potential is unchanged, and furthermore the applied potential must be taken symmetrical about the slab center.

[8] See Ref. 1, p. 231.

[9] J. R. Smith, S. C. Ying, and W. Kohn, Phys. Rev. Lett. 30, 610 (1973).

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