Screening Properties of a Metal Surface at Low Frequencies and Finite Wave Vectors

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The local-density scheme is used to calculate the self-consistent electron density of a semi-infinite metal in the presence of a static external field of finite wave vector $\mathbf{q}_{\parallel}$. The total electrostatic potential is used to determine the rate of exciting electron-hole pairs at low frequencies. The lifetime of the CO stretch vibration on Cu is calculated and the intensity of inelastically scattered electrons is predicted for finite momentum transfers.

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During recent years, considerable progress has been made in the understanding of the dynamical response of metal surfaces to external electromagnetic fields. The most realistic calculations for semi-infinite systems have been carried out in the long-wavelength limit by Feibelman[1] at high frequencies and by Persson and Andersson[2] in the low-frequency regime. Dobson and Harris[3] presented results for the static, finite-wave-vector susceptibility. So far, the only calculation of the response at finite frequencies and nonzero wave vectors was performed by Eguiluz[4] for thin metal films. In all cases, the jellium model was used in which the positive ion cores are replaced by a uniform background.

The purpose of the present work is twofold: First, the local-density scheme is used to determine the self-consistent response of a semi-infinite jellium metal to a static external field of finite wave vector $\mathbf{q}_{\parallel}$. Of particular interest is the shift of the centroid of the induced density and the reduction of its overall weight as the magnitude of the wave vector increases. Second, the self-consistent total electrostatic potential is used in the golden-rule formula to calculate the power absorption due to the creation of electron-hole pairs. These results are important for a wide variety of surface-related phenomena involving low excitation energies and arbitrary momentum transfers. As an application, the inelastic electron scattering probability is determined as a function of wave vector. Furthermore, the lifetime of the CO stretch vibration on Cu(100) is calculated and compared with experiment. A previous theoretical estimate[4] of this quantity, obtained within the random-phase approximation (RPA) of the dynamical response, is shown to be unreliable since the use of the RPA in conjunction with a local-density ground-state calculation does not satisfy the exact force sum rule.

An arbitrary electric potential outside the metal may be expressed as a superposition of evanescent plane waves of the form:

$$\phi_{\mathrm{ext}}(\mathbf{q}_{\parallel},\omega)=\phi_0 e^{qz}\exp[i(\mathbf{q}_{\parallel}\cdot\mathbf{r}_{\parallel}-\omega t)]+\mathrm{c.c.} \tag{1}$$

where $q=|\mathbf{q}_{\parallel}|$ and the metal occupies the half-space $z<0$. For sufficiently weak fields, the potential induced by (1) may be written for large z as

$$\phi_{\mathrm{ind}}(\mathbf{q}_{\parallel},\omega)=-\phi_0 g(q,\omega)e^{-qz}\exp[i(\mathbf{q}_{\parallel}\cdot\mathbf{r}_{\parallel}-\omega t)]+\mathrm{c.c.}$$

The amplitude factor $g(q,\omega)$ is related to the rate w at which the external potential (1) excites electron-hole pairs in the metal[2,5] through

$$\mathrm{Im}\,g(q,\omega)=\pi\hbar\, w(q,\omega)/Aq \tag{2}$$

where A is the surface area. w may be calculated using the golden-rule formula:

$$w(q,\omega)=2(2\pi/\hbar)\int d^3k\int d^3k' f_k(1-f_{k'})|\langle \mathbf{k}'|e\phi|\mathbf{k}\rangle|^2\delta(\epsilon_{k'}-\epsilon_k-\hbar\omega), \tag{3}$$

where the factor of 2 accounts for the electron spin, ϵ_k and $\psi_{\mathbf{k}}\sim\exp(i\mathbf{k}_{\parallel}\cdot\mathbf{r}_{\parallel})\psi_{k_z}(z)$ are the one-electron energies and eigenstates of the semi-infinite jellium metal in the absence of the field, and f_k are occupation numbers. At low frequencies the total (complex) potential ϕ may be approximated by its static limit, $\phi(\mathbf{q}_{\parallel},\mathbf{r})=\phi(q,z)\exp(i\mathbf{q}_{\parallel}\cdot\mathbf{r}_{\parallel})$, where

$$\phi(q,z)=\phi_0\exp(qz)+\phi_{\mathrm{ind}}(q,z)$$

and ϕ_{ind} is related to the induced surface density $\sigma(q,z)$ by

$$\phi_{\mathrm{ind}}(q,z)=(2\pi/q)\int dz'\exp(-q|z-z'|)\sigma(q,z').$$

The presence of the external potential amounts to a periodic perturbation of the one-electron states which, as a result, acquire two-dimensional Bloch character in the vicinity of the surface with reciprocal-lattice vectors given by multiples of $\mathbf{q}_{\parallel}$. In the present work, this problem is solved self-consistently by use of the local-density approximation. For the exchange-correlation energy the Wigner formula is used in order to be able to compare results to those of Lang and Kohn[6] in the $q=0$ limit. Both the ground-state density and the surface density induced by a uniform electric field were found to be in excellent agreement with those calculated by these authors for several values of r_s. {Atomic units are used, i.e, $r_s=[3/(4\pi n)]^{1/3}$ where n is the bulk density.}

In Fig. 1, the profile of the induced density $\bar\sigma(q,z)=(2\pi/q\phi_0)\exp(-qz_0)\sigma(q,z)$ is shown for $q=0.5k_F$ and $r_s=2$. Here, k_F is the Fermi momentum and z_0 is the centroid of the induced density in the $q=0$ limit. This normalization is chosen so that the external potential at z_0 is $2\pi/q$, i.e., unit external charges producing $\phi_{\rm ext}$ would induce unit surface charges at z_0 if perfect image theory would hold. $\bar\sigma$ is seen to differ from the corresponding $q=0$ distribution in several important ways: The centroid is shifted slightly towards the surface, the integrated weight is reduced, and the wavelength of the Friedel oscillations is enhanced. The smallness of the shift of the centroid is consistent with earlier variational calculations[7] indicating that the position of the image plane is well given by z_0 even for charges as close as 3 to 4 a.u. to the surface. The reduction of weight amounts to about 20% for the case shown in Fig. 1 and increases rapidly for larger q, suggesting sizable deviations from perfect images. This decrease of the induced surface density may be interpreted as incomplete screening of the oscillatory external potential. The enhancement of the periodicity of the Freidel oscillations by about 3% for $q=0.5k_F$ agrees well with the theoretically expected[3] reduction of the parameter $\alpha=2k_F$ at $q=0$ to $\alpha=(4k_F^2-q^2)^{1/2}$ caused by the finite Fourier components of the perturbed eigenstates.

The total electrostatic potentials corresponding to the surface densities shown in Fig. 1 are plotted in Fig. 2. The same normalization is chosen, i.e., $\bar\phi(q,z)=(2\pi/q\phi_0)\exp(-qz_0)\phi(q,z)$. As expected, inside the metal the amplitude of the Friedel oscillations for $q>0$ is reduced and their wavelength is enhanced. Also, the surface sum rule,[8] which requires the total electrostatic potential produced by a uniform field to vanish at the jellium edge, does not apply in the case $q>0$, so that $\bar\phi(q>0,z=0)\neq 0$. Outside the metal, the potentials are remarkably similar up to about $z=3$ a.u. Beyond this distance, $\bar\phi$ is dominated by the rapidly growing external potential.

In the limit of small frequencies, the surface contribution to the transition rate (3) can be reduced to the simple form[2,9]

$$w(q,\omega)=2\phi_0^2q^2A\,\omega(\pi\hbar k_F\omega_p)^{-1}\xi(q)$$

where ω_p is the plasma frequency. From (2) one therefore has

$$\operatorname{Im}g(q,\omega)=2q\,\omega(k_F\omega_p)^{-1}\xi(q),$$

where

$$\xi(q)=\omega_pk_F\pi^{-4}\int_0^{k_F}dk_z\int_0^{\pi}d\Phi\,k_z'^{-1}|\langle k_z'|\bar\phi|k_z\rangle|^2 \qquad (4)$$

with $k_z'=(k_z^2-2kq\cos\Phi-q^2)^{1/2}$ and $k=(k_F^2-k_z^2)^{1/2}$. Thus, at low frequencies, the quantity $\operatorname{Im}g(q,\omega)$, which is of central importance in many surface phenomena, is linear[10] in ω and its momentum dependence is entirely governed by the function $\xi(q)$. The variation of $\xi(q)$ with momentum is shown in Fig. 3 for $r_s=2$ and 3. These results are compared with $\xi_0(q)$ which is obtained if $\bar\phi(q,z)$ in (4) is approximated by its long-wavelength limit. In this case, the q dependence of $\xi_0(q)$ arises from the fact that k_z' depends on q. The comparison demonstrates that for $q/k_F\gtrsim 0.25$, $\xi_0(q)$ underestimates the actual magnitude of $\xi(q)$ by up to a factor of 2.

As has been shown by Persson,[11] the inelastic scattering probability for low-energy electrons is,

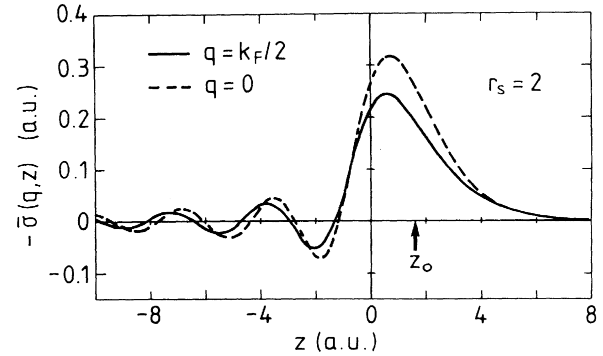

FIG. 1. Surface density induced by static external field of wave vector q. The metal occupies the half-space $z<0$. The position of the image plane for $q=0$ is denoted by z_0.

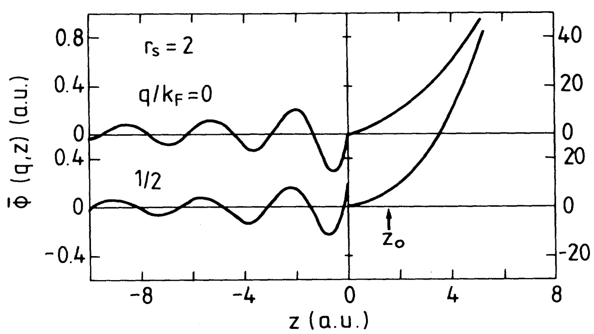

FIG. 2. Total electrostatic potentials corresponding to induced densities shown in Fig. 1. Note the different scales for positive and negative z.

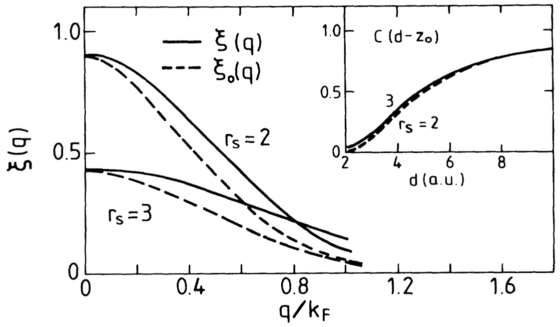

FIG. 3. Momentum dependence of the functions $\xi(q)$ and $\xi_0(q)$ (see text) for $r_s = 2$ and 3. The inset shows the function C defined in (6).

within the dipole approximation, proportional to $\mathrm{Im}\,g(q,\omega)$. Therefore, the results shown in Fig. 3 are of direct relevance to the interpretation of loss spectra away from specular scattering. It would be of great interest to experimentally verify the calculated variation of the inelastic scattering intensity with momentum transfer.

Other surface problems which are essentially determined by $\mathrm{Im}\,g(q,\omega)$ are the friction force felt by a heavy charged particle moving above a metal surface, the van der Waals interaction potential, and the damping of a vibrating dipole of an adsorbed molecule. In the last case, the lifetime is given by[2]

$$\tau^{-1} = 1.5\mu^2\omega(k_F\omega_p)^{-1}\xi(0)(d-z_0)^{-4}C(d-z_0), \tag{5}$$

where d is the position of the (point) dipole and

$$C(z) = \tfrac{8}{3}z^4\int_0^\infty dq\,q^3 e^{-2qz}\xi(q)/\xi(0). \tag{6}$$

The above factorization of τ^{-1} is convenient since $C(z) \to 1$ for large z and $C(z) \equiv 1$ if $\xi(q)$ is approximated by its long-wavelength limit, $\xi(0)$. The variation of $C(d-z_0)$ as a function of d is shown in the inset of Fig. 3.

The lifetime of the CO stretch vibration on Cu(100) has been calculated by various methods, the most detailed of which is that by Eguiluz[4] for thin jellium films. Using $\mu = 0.25$ D, $\omega = 0.25$ eV, and $d = 1.6$ Å, he obtains $\tau = 9\times10^{-12}$ sec. With these parameters and $r_s = 2.67$, $z_0 = 1.4$ a.u., and $\xi(0) = 0.55$ for Cu, expression (5) gives instead $\tau = 5\times10^{-12}$ sec. The reason for the discrepancy between these results is most likely the fact that, in the present work, both the ground state of the semi-infinite metal and its response to the external field are based on a consistent description of exchange and correlation. In Ref. 4, however, the ground-state wave functions of the jellium slab are obtained from a local-density calculation whereas the dynamical response is treated within the RPA. It can be easily be shown,[12] that this implementation of the RPA, which had also been used in other surface response calculations,[13] implies an inconsistent description of exchange and correlation and therefore does not satisfy the exact force sum rule for static uniform fields.[8] A particular consequence of this is a sizable shift of the image plane towards the surface.[14] For Cu and $q = 0$, the inward-shift amounts to 0.4 a.u. Since, according to (5), the vibrational lifetime is proportional to the fourth power of the distance of the dipole from the image plane, it is evident that the RPA leads to a drastic overestimate of the lifetime.

Another reason for the difference might be that, for the assumed position of the dipole, the CO molecule is located in the tails of the Cu valence density and not entirely outside as was implicitly assumed in the present work. Incorporation of this effect, which is to some extent built into the scheme by Eguiluz, will presumably give rise to a slightly larger lifetime than obtained from (5).

As indicated by several measurements,[15] the actual dynamical dipole moment for CO on Cu(100) is about 0.2 D, giving accordingly larger lifetimes: 8×10^{-12} sec in the present work and 14×10^{-12} sec in Ref. 4. The width of the experimental absorption line,[16] on the other hand, is considerably larger, giving $\Gamma^{-1} = 1.3\times10^{-12}$ sec. While the electron-hole pair mechanism discussed above is certainly present, it has been estimated[17] to be less important than the damping associated with the partial filling of the antibonding $2\pi^*$ level during the molecular vibration. Lifetime measurements on less strongly adsorbed molecules would therefore be desirable. Other mechanisms, such as dephasing, inhomogeneous broadening, etc., might also contribute to the observed linewidth.

In summary, the electron density induced at the surface of a semi-infinite metal in the presence of a periodic static electric field has been evaluated for the first time. With the assumption that, at low excitation energies, the real part of the total potential is reasonably well represented by its static form, the rate of exciting electron-hole pairs is calculated as a function of momentum transfer. Since a fully dynamical, finite-wave-vector response calculation for a semi-infinite metal is not yet available, the present results should be useful for interpretation of various surface experiments involving small frequencies, but arbitrary momentum transfers.

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[9] At finite frequencies, there is, of course, also a volume contribution to the transition rate and a surface-volume interference term (see Refs. 2 and 5). In the following I focus on the surface contribution. A more detailed account of the present work and the evaluation of the bulk and interference terms will be given in a subsequent publication.

[10] Excellent linear behavior was found in Ref. 4 for excitation energies up to 1 eV.

[11] B. N. J. Persson, Phys. Rev. Lett. **50**, 1089 (1983).

[12] The RPA treatment in Ref. 4 is, in fact, equivalent to a self-consistent Hartree calculation with the ground-state exchange-correlation potential $v_{\mathrm{xc}}(z)$ included as a density-independent, external potential. Instead of the exact sum-rule condition (Ref. 8) $\bar{\phi}(z=0)=0$ for $q=0$, one obtains $n\bar{\phi}(z=0)=-\int_{-\infty}^{\infty}dz\,\bar{\sigma}(z)\,dv_{\mathrm{xc}}(z)/dz$ where n is the bulk density.

[13] See, e.g., Ref. 1 and other references cited herein.

[14] A similar shift relative to the static, $q=0$ position of the image plane is also seen at frequencies near $0.5\omega_p$ (see Ref. 1).

[15] See, e.g., S. Andersson and B. N. J. Persson, Phys. Rev. Lett. **45**, 1421 (1980).

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