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Local-density-functional calculation of electrodynamic surface response

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A frequency-dependent exchange-correlation potential is employed to calculate the nonlocal effects on the optical response of jellium-metal surfaces within a microscopic self-consistent model. Results for the frequency-dependent surface-response function $d_\perp$ for the whole range of metallic densities are presented. In context with electrochemical experiments, the electric field effect on the differential reflectance is studied.

Recently we have studied the electromagnetic response of jellium-metal surfaces, using a microscopic nonlocal theory based on the random-phase approximation (RPA).[1] We concentrated on the so-called nonlocal optical effects, which occur owing to the spread of optically induced charges at the metal surface. These effects, which cannot be described in the framework of classical Fresnel optics, contain detailed information about the electronic surface structure. This is why optical methods, such as difference reflection spectroscopy or ultraviolet photoemission, have attracted outstanding interest. An adequate survey of the theory of surface electromagnetic fields may be found in two recent review articles.[2,3]

In our model,[1] the ground-state electronic density is treated in the self-consistent density-functional formalism elaborated by Lang and Kohn.[4] This formalism allows a consistent description of the electromagnetic surface response, since the RPA comprises electron-hole pair and collective plasma excitations, and the detailed electronic structure at the surface is taken into account. A shortcoming of the RPA treatment is, however, that exchange and correlation effects are not readjusted to the responding electronic system. To get rid of this discrepancy, a generalized linear-response theory, which takes into account the static exchange-correlation potential, has been proposed,[5] and various applications to surface-response problems have been presented.[6,7]

An actual frequency-dependent linear-response theory, with a corresponding frequency-dependent exchange-correlation potential has been developed by Gross and Kohn.[8] The key equation which they derived for the self-consistently induced electron density can be written as

$$\begin{aligned}\delta n(\mathbf{K},z;\omega)=\int dz'\chi^{(0)}(\mathbf{K},z,z';\omega)\\ \times[\Phi_{\mathrm{sc}}(\mathbf{K},z';\omega)\\ +f_{\mathrm{xc}}(\omega\,|\,n(z'))\delta n(\mathbf{K},z';\omega)]\ . \end{aligned}\tag{1}$$

Here, the nonlocal dependence in the direction parallel to the metal surface is dissolved by Fourier transformation, $\mathbf{K}$ denotes the two-dimensional parallel momentum vector, ω the frequency, and the z axis is chosen perpendicular to the surface. $\chi^{(0)}$ denotes the density-density response function of the unperturbed ground state, and Φ_{sc} is the self-consistent electrostatic potential, which fulfills Poisson's equation:

$$\frac{d^2}{dz^2}\Phi_{\mathrm{sc}}(z;\omega)=\frac{d^2}{dz^2}\Phi_{\mathrm{ext}}(z;\omega)-4\pi e^2\delta n(z;\omega)\ ,\tag{2}$$

with Φ_{ext} the external applied potential. [For convenience, the $\mathbf{K}$ dependence in Eq. (2) is not written in full.] A local exchange-correlation term, which is linear in the induced density δn, emerges in Eq. (1). Omitting this term ($f_{\mathrm{xc}}=0$) yields the conventional RPA response referred to before. In the spirit of local-density approximation, Gross and Kohn[8] give a parametrization of the function f_{xc} by a Padé-type expression, depending on the exchange-correlation energy per particle of a homogeneous electron gas, $\varepsilon_{\mathrm{xc}}$. Asymptotically for zero and for high frequency the following relations hold:[8]

$$f_{\mathrm{xc}}(\omega=0\,|\,n)=\frac{d^2}{dn^2}[n\varepsilon_{\mathrm{xc}}(n)]\ ,\tag{3}$$

$$f_{\mathrm{xc}}(\omega\rightarrow\infty\,|\,n)=-\tfrac{4}{3}n^{2/3}\frac{d}{dn}[n^{-2/3}\varepsilon_{\mathrm{xc}}(n)]\ .\tag{4}$$

Furthermore, $f_{\mathrm{xc}}(\omega)$ is a complex-valued function, which is analytic in the upper half of the complex ω plane, and satisfies the Kramers-Kronig relations.[8]

Within this theory we have calculated the nonlocal effects on the optical response of metal surfaces, i.e., the linear response to an electromagnetic wave in oblique incidence. In solving Maxwell's equations, the essential simplification follows from a long-wavelength expansion.[3] It takes advantage of the fact that the external field and the induced longitudinal field vary on different length scales, given by the wavelength of light and the (much smaller) Fermi wavelength, respectively. In this limit, Maxwell's equations are effectively decoupled, and the interesting nonlocal effects can be summarized in two surface-response functions $d_\parallel, d_\perp$.[3] In our model,[1] $d_\parallel$ is given by the zeroth momentum of the electron density,

$$d_\parallel = \frac{1}{n_+}\int dz[n(z)-n_+\Theta(z-z_b)]\ , \tag{5}$$

with $n_+\Theta(z-z_b)$ the jellium density, Θ the unit step function, and $d_\perp$ is determined by the center of mass of the optically induced charge,

$$d_\perp = \int dz(z-z_b)\delta n(z;\omega)\Big/\int dz\delta n(z;\omega)\ . \tag{6}$$

In calculating these surface-response functions, the small parallel momentum vector $\mathbf{K}$ can be neglected owing to the long-wavelength limit. Other optical quantities can be expressed through these functions, e.g. the reflection amplitude for p-polarized light:[3]

$$r_p = \frac{\epsilon_t p - p_t - i(1-\epsilon_t)(pp_t d_\parallel - K^2 d_\perp)}{\epsilon_t p + p_t - i(1-\epsilon_t)(pp_t d_\parallel + K^2 d_\perp)}\ . \tag{7}$$

Here, the normal components of the incident and the transverse transmitted wave vector are denoted by p and p_t, respectively, $K=|\mathbf{K}|$, and we introduced a free-electron-like dielectric constant $\epsilon_t = 1-\omega_p^2/\omega^2$, with $\omega_p=(4\pi n_+ e^2/m)^{1/2}$ the bulk plasma frequency, e the electronic charge, and m the electronic mass.

In the numerical calculations we have used a finite jellium slab model, owing to computational convenience.[1] After solving the Kohn-Sham equations for the ground-state electronic density self-consistently,[9] we used a special Fourier representation[1,7] to obtain the density-density response. An improved approximation for the exchange-correlation energy ε_{xc} was incorporated.[10] In calculating the response function $d_\perp$, a phenomenological damping constant γ has been included.[11]

In Fig. 1, the result for the surface-response function $d_\perp$ is shown for different metallic densities, given by the Wigner-Seitz radius $r_s=(\frac{1}{3}4\pi n_+ a_0^3)^{-1/3}$, with a_0 the Bohr radius. Compared with the result of the conventional RPA,[1,3] our density-functional calculation yields noticeably more negative values for the real part of $d_\perp$. Since the exchange-correlation interaction is calculated on equal footing both in the ground state and in the response, the values of $d_\perp$ in the static limit ($\omega \rightarrow 0$) agree with the center of mass of the static induced charge, obtained from a ground-state calculation.[12] The imaginary part of $d_\perp$ is, in the low-frequency region, linear in ω, and is likewise more negative than the RPA result. Our results for $d_\perp(\omega\rightarrow 0)$ and for the linear coefficient of the imaginary part $\mathrm{Im}d_\perp(\omega\rightarrow 0)=\xi(\omega/\omega_p)$ agree with those calculated by Liebsch[6] for $r_s=2,3,4$.[13] At higher frequencies no serious differences between the two theories are discernable, so that our prevous interpretation of the optical response[1] can be maintained. We conclude that the effect of the exchange-correlation interaction is important at moderate frequencies, but negligible in the high-frequency regime.

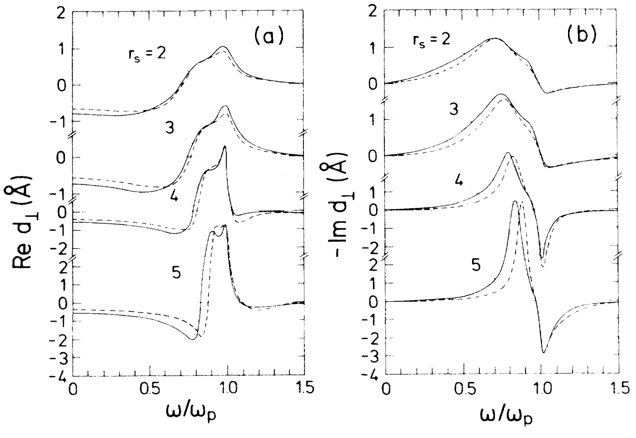

FIG. 1. (a) Real and (b) negative imaginary part of the surface response function $d_\perp$ vs frequency. Solid lines: present calculation with frequency-dependent exchange-correlation interaction. Dashed lines: conventional RPA. The parameters used in the computations are jellium slab thickness, 48, 60, 90, and 100 Å, damping constant $\gamma/\omega_p = 0.06, 0.05, 0.02, 0.02$, for $r_s=2,3,4,5$, respectively. Note that for $r_s=4,5$ the scale is different than for $r_s=2,3$. The estimated numerical accuracy is ±0.05 Å.

Finally we briefly discuss, as an interesting application, the electric field effect on the differential reflectance,[14] i.e., the relative change of the reflectance $R=|r_p|^2$ for differently charged metal surfaces,

$$\Delta R/R = [R(\sigma+\Delta\sigma)-R(\sigma)]/R(\sigma)\ . \tag{8}$$

with σ the surface charge (per unit area).[15] In Fig. 2 we show typical results for the differential reflectance of a metal surface with the surface charge varied from the cathodic (curve 1) to high anodic (curve 7) values. Apparently, the peak structure in $-\Delta R/R$ shifts towards the plasma frequency and becomes sharper, but finally

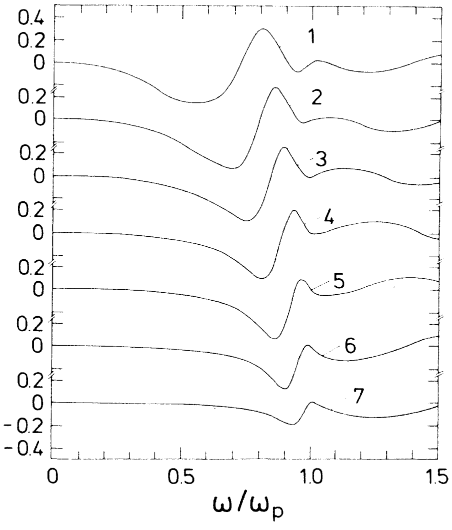

FIG. 2. Field effect on the differential reflectance for a metal surface with $r_s=3$ and surface charge σ (in μC/cm^2): curve 1, -3.8; curve 2, 0; curve 3, 3.8; curve 4, 7.6; curve 5, 15.3; curve 6, 22.9; and curve 7, 30.6. The change in surface charge is $\Delta\sigma = 7.6\ \mu$C/cm^2 and the angle of incident light is 45°.

decreases. Since this effect is a result of the dramatic changes in the surface-response function $d_\perp$,[7] it appears only for p-polarized incident light.

Direct comparison of this field effect with conventional electrochemical experiments, e.g., at silver electrodes,[14] is not conclusive, since the experimental results depend largely on the electronic band structure. However, for free-electron metals, which can be studied in nonaqueous electrolytes, the above theory is well established. Experimental confirmation of the field effect would provide a better understanding of the microscopic surface response properties.

Note added in proof. Recently, a correction to Eq. (4) was published,[16] which, however, does not change our results significantly.

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[15] Compare Eq. (5); a change in the surface charge by $\Delta\sigma$ is equivalent to a change in $d_\parallel$ by $\Delta\sigma / |e| n_+$.

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