Variational Calculation of the Surface-Plasmon Dispersion Relation for a Metal*

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We have computed the surface-plasmon dispersion relation for a metal and compared it with experimental results for Al and Mg. The metal surface is approximated by a step potential and the calculation carried out within the quantum-mechanical random-phase approximation. The integral equation for the self-sustained oscillations is handled by a variational approach. Our dispersion relation is in much better agreement with experimental results than the relation computed for a semi-infinite electron gas.

The dispersion relation for the surface plasmon plays an important role in the analysis of the inelastic low-energy electron diffraction (ILEED) data.[1] Recent experimental data[1,2] indicate that the coefficient of the term linear in parallel momentum in the dispersion relation is negative. Microscopic calculations[3,4] for a semi-infinite electron gas with a perfectly reflecting boundary give a positive coefficient for the linear term in contrast to the experimental evidence. It has been suggested that the shape of the surface potential, or equivalently the density profile at the surface, plays an important role in determining the surface-plasmon dispersion relation.[5-7] Using a hydrodynamic model with a variable electron-density profile, Bennett[6] has been able to account for Kunz's experimental data for Mg.[2] It is not clear, however, that the hydrodynamic approximation is justified, and a first-principles calculation for a realistic surface potential with no adjustable parameters is of interest.

We report here a microscopic calculation of the surface-plasmon dispersion relation where the metal surface is represented by a finite step potential

$$V_0(z) = \begin{cases} 0, & z<0, \\ W+E_{\mathrm{F}}, & z>0. \end{cases} \tag{1}$$

where W is the work function and $E_{\mathrm{F}} = \hbar k_{\mathrm{F}}^2/2m$ is the Fermi energy of the metal. The calculation is carried out within the random-phase approximation (RPA).

The charge-density response of the system is related to the total electric potential V by the equation

$$\rho(Q,z;\omega) = \int dz'\, L(Q,z,z';\omega)\, V(Q,z'), \tag{2}$$

where $\vec{Q}$ is the component of momentum parallel to the surface and ω is the frequency. Within the RPA the general form of the linear response function $L(Q,z,z';\omega)$ is well known.[3,5] In the following, we shall carry all calculation to second order in Q. Accordingly, we expand L and obtain[8]

$$\begin{aligned} L(Q,z,z';\omega) = {} & 4me^2 \sum_{k_z} f(|k_z|)(k_{\mathrm{F}}^2 - k_z^2)\psi_{k_z}{}^*(z)\psi_{k_z}(z')\left[1+\tfrac{1}{2}Q^2(k_{\mathrm{F}}^2-k_z^2)\,\partial^2/\partial(2m\hbar\omega)^2\right] \\ & \times \sum_{k_z'} \psi_{k_z'}(z)\psi_{k_z'}{}^*(z')\left[(k_z^2-k_z'^2-Q^2+2m\hbar\omega)^{-1}+(k_z^2-k_z'^2-Q^2-2m\hbar\omega)^{-1}\right]+O(Q^4/\omega^2). \end{aligned} \tag{3}$$

Here $\psi_{k_z}(z)$ is a solution of the one-dimensional Schrödinger equation for the potential given in (1), and $f(|k_z|)$ is the zero-temperature Fermi function which vanishes for $|k_z|>k_{\mathrm{F}}$. In Eq. (3) the summation over k_z' yields the Green's function of a single electron in the potential (1), which is easily computed.

The electric potential in a charged system is also related to the charge density by Poisson's equation[9] which can be written

$$V(Q,z;\omega) = (2\pi/Q)\int_{-\infty}^{\infty} dz'\, e^{-Q|z-z'|}\rho(Q,z';\omega). \tag{4}$$

Equations (2) and (4) can be combined to form a homogeneous integral equation for ρ which determines the self-sustained oscillations of the system.

The kernel of the integral equation is Lf_Q, where $f_Q(z,z') = 2\pi e^{-Q|z-z'|}/Q$, and the solutions to the eigenvalue problem

$$Lf_Q|u\rangle = \lambda|u\rangle, \quad \lambda = 1,$$

are solutions of the homogeneous equation. For complex values of ω, $L^{\dagger}(\omega)=L(\bar{\omega})$ where $\bar{\omega}=-\omega^*$ (a star indicates the complex conjugate). It can be shown that,[10] if $|u(\omega)\rangle$ is a right eigenvector of Lf_Q, then $\langle u(\bar{\omega})|$ is a left eigenvector of $f_Q L$, with the same eigenvalue. Therefore the functional form

$$\lambda(\omega)=\frac{\langle u(\bar{\omega})|f_Q L f_Q|u(\omega)\rangle}{\langle u(\bar{\omega})|f_Q|u(\omega)\rangle}=\frac{\langle v(\bar{\omega})|L|v(\omega)\rangle}{\langle v(\bar{\omega})|f_Q^{-1}|v(\omega)\rangle}, \tag{5}$$

where $|v(\omega)\rangle = f_Q|u(\omega)\rangle$ and $f_Q^{-1}(z,z')=[Q^2-\partial^2/\partial z^2]\delta(z-z')/4\pi$,[5] is stationary, if and only if $|v(\omega)\rangle$ is an eigenvector of L. Thus we have a variational principle for the determination of λ. The procedure is to choose a functional form for the potential $|v\rangle$ which depends on variational parameters and to adjust the parameters and complex frequency ω in order to satisfy the conditions $\lambda(\omega(Q))=1$, $\delta\lambda/\delta|v(\omega)\rangle=0$, and $\delta\lambda/\delta\langle v(\bar{\omega})|=0$.

To gain some insight into the choice of variational functions,[11] notice that if ω is chosen to be pure imaginary and positive, then $\bar{\omega}=\omega$ and L is Hermitian. A knowledge of the spectrum of Hermitian operators leads one to expect there is an isolated eigenvalue which is associated with a localized charge distribution with no nodes. This eigenvalue continues to complex frequencies and must be the one that gives rise to the surface plasmon on physical grounds.

Hence, we have chosen (α being a complex variational parameter)

$$v_s(z;\omega)=\frac{2\pi}{Q}\begin{cases} e^{Qz}, & z<0,\\ e^{-\alpha z}, & z>0,\end{cases} \tag{6}$$

for the potential function, which corresponds to the charge distribution

$$u_s(z;\omega)=\tfrac{1}{2}\begin{cases} 0, & z<0,\\ (1+\alpha/Q)\delta(z)+(Q^2-\alpha^2)e^{-\alpha z}/Q, & z>0.\end{cases}$$

The dependence on ω is implicit in α; $u_s(z,\bar{\omega})$ will contain $\beta=\alpha(\bar{\omega})$. For this potential form, $\lambda_s(\beta^*,\alpha)=\lambda_s(\alpha,\beta^*)$ so that $\beta^*=\alpha$ at the stationary point, and one can analytically perform all of the integrals for λ and L, Eqs. (3) and (5), except for one integration over the finite interval $-k_{\mathrm{F}}<k_z<k_{\mathrm{F}}$, which is performed numerically. For imaginary ω, λ_s has a minimum for α real and $\alpha\lesssim Q$.

Evaluating (5) in the lower half of the complex ω plane where $\lambda(\omega_s(Q))=1$, we find that $\mathrm{Re}\lambda_s$ is a maximum and $\mathrm{Im}\lambda_s$ has a saddle point at $\delta\lambda/\delta\alpha=0$. Since $\mathrm{Re}\lambda_s$ is a maximum and $\lambda\sim\omega^{-2}$ for small Q, we obtain a lower bound for the real part of the dispersion relation. At the maximum, $\mathrm{Re}\alpha_m\lesssim Q$ and $\mathrm{Im}\alpha_m$ is small and negative.

The leading term in the dispersion relation for $\omega_s(Q)$ is $\omega_{s0}=\omega_p/\sqrt{2}$, where ω_p is the bulk-plasmon frequency. The coefficients in the dispersion relation

$$\frac{\omega_s(Q)}{\omega_{s0}}=1+i\Gamma_0+(A_1+iA_2)\frac{Q}{k_{\mathrm{F}}}+(B_1+iB_2)\left(\frac{Q}{k_{\mathrm{F}}}\right)^2 \tag{7}$$

are given in Table I for an electron density which corresponds to Al. The parameters[12] used in (2) are $E_{\mathrm{F}}=11.64$ eV, $W=4.19$ eV, and $\hbar\omega_p=14.2$ eV (this is the value of $\hbar\omega_p$ needed by Bagchi *et al.* to fit their ILEED data).[1] The experimentally determined coefficients[1] and RPA results for the semi-infinite electron gas[3] are presented in Table I for comparison.

We have also obtained the dispersion relation

$$\frac{\omega_s(Q)}{\omega_{s0}}=1+(-0.234+0.244i)\frac{Q}{k_{\mathrm{F}}}+(2.02+0.95i)\left(\frac{Q}{k_{\mathrm{F}}}\right)^2$$

for Mg using[12] $E_{\mathrm{F}}=7.13$ eV, $W=3.66$ eV, and $\hbar\omega_p=10.60$ eV. The real part of this expression is plotted in Fig. 1 for comparison with Kunz's data[2] (Kunz quotes a value of $\hbar\omega_{s0}=7.3$ eV which has been used to normalize his data, plotted in Fig. 1). For comparison, the RPA result for the semi-infinite gas[3] is

$$\frac{\omega_s(Q)}{\omega_{s0}}=1+(0.455+0.009i)\frac{Q}{k_{\mathrm{F}}}+(0.776+0.027i)\left(\frac{Q}{k_{\mathrm{F}}}\right)^2;$$

the real part of this expression is also plotted in Fig. 1.

In order to assess the accuracy of the results obtained, one should perform the computation us-

TABLE I. Coefficients for Al in the expansion of $\omega_s(Q)$ for small Q, Eq. (7).

Source	A_1	B_1	Γ_0	A_2	B_2
This calculation	−0.122	2.53	0	0.358	1.09
Bagchi *et al.*[a]					
Preferred	−0.12	3.0	0.15	0.13	···
Acceptable	0.09	1.8	0.16	0.13	···
Semi-infinite[b] RPA	0.602	0.992	0	0.013	0.043

[a] Ref. 1.

[b] Ref. 3.

ing a variety of trial functions. It is difficult to find acceptable trial functions which allow Eq. (5) to be analytically reduced to a single integration over a finite interval. The reduction is possible for $u_s(z;\omega)=\delta(z-a)$, where a is the variational parameter. One cannot satisfy the extremum condition $\delta\lambda/\delta|u(\omega)\rangle=0$ with the single real variational parameter a, since $\lambda(\omega)$ is complex. However, for very small Q ($\lesssim 0.1k_\mathrm{F}$) we find that the extremum condition is "almost" satisfied for $a\simeq -0.5/k_\mathrm{F}$ and that the value of $\lambda(\omega)$ is almost the same as we found using the trial function given in Eq. (6).

The agreement between the theoretical and experimental results for the $\mathrm{Re}\,\omega_s$ is excellent for Al,[1] but not nearly so good for the Mg data.[2] However, the experimental uncertainties are large, and the agreement is greatly improved over the semi-infinite electron-gas relation.[3]

The value $\Gamma_0=0$ is independent of the trial function, since $\lambda_s(\omega)\to\omega_p{}^2/2\omega^2$ as $Q\to 0$. Hence, one needs to attribute the experimental values of Γ_0 to some other features, such as band effects and surface scattering, that have not been included in the present treatment.

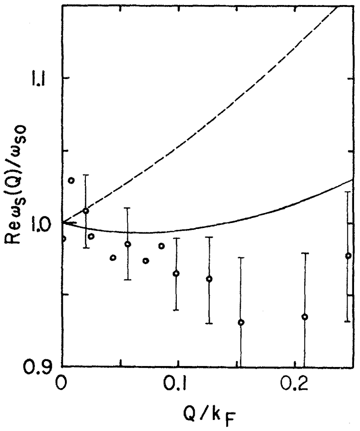

FIG. 1. Real part of $\omega_s(Q)/\omega_{s0}$ as a function of Q/k_F for Mg. Solid curve, present calculation; dashed curve, semi-infinite electron-gas calculation reported in Ref. 3; experimental points, from the data of Kunz, Ref. 2.

The theoretical value for the coefficient A_2 of $\mathrm{Im}\,\omega_s$ is in order-of-magnitude agreement with the value needed to fit the experimental results for Al.[1] Since the method used for the fitting does not give a precise estimate of A_2,[1] there is no clear disagreement with experiments for any of the computed coefficients. This is a definite improvement over the results of the calculation for the semi-infinite medium. An analysis of semiconductor tunneling data[13] indicates that A_2 should be 10 to 20 times larger than the RPA value for a semi-infinite electron gas. This is consistent with the present calculation, and with the values obtained by Feibelman[5] for a surface model with a step in the density profile. Feibelman's value for Al would be $A_2=0.227$. Since we have used a realistic model for a metal surface which produces results for $\mathrm{Re}\,\omega_s$ in good agreement with experiment, we feel that the values for A_2 and B_2 quoted here are the best values that are presently available for these coefficients.

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