The values we have obtained for positions of core levels, their splittings and for conduction-band widths are given in Table I along with values obtained by other workers. Values obtained in the analysis of different experimental runs fall within 0.1 eV of the central values indicated, and thus well within the quoted error limits. The quoted experimental errors result from broadening of structural features by the resolution of the energy analyzer, and in the case of E_a and E_b from the precision with which we can set the energy scale. We have assumed that positions of structural features can normally be determined to within a fifth of the uncertainty in the width of the distribution.

In our analysis of the data we have assumed that the core-level energy positions are the same in the photoexcitation and Auger recombination processes. This implies that the final state of the Auger process is the same as the initial state of the excitation, i.e., that it results in a lattice ion in its "ground-state" configuration. This could not be true for an atom in which the Auger process leaves the atom in an ionized state. Our assumption implies that the electron excited in the Auger process in a metal is removed from the Fermi sea and does not significantly change the electron environment surrounding the ion deexcited by the Auger process. The failure of this assumption would add additional error to the values of E_a and E_b but not to their differences.

Error limits on values of E_F in Table I are those imposed by the resolution of our experimental data. Additional uncertainties in E_F may result from our use of a very simple model in the Auger peak analysis.

Our values of the spin-orbit splitting between $^2P_{3/2}$ and $^2P_{1/2}$ core levels agree with those observed in optical data from singly ionized Rb and Cs. They do not agree well with the values observed in optical data from neutral Rb and Cs with the atomic configurations $np^5(n+1)s^2$. This indicates that any valence electron relaxation effects that accompany the excitation of the core electrons do not substantially change the spin-orbit splittings from those observed in the free ion.

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Photon Interactions at a Rough Metal Surface*

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We have analyzed the processes of diffuse scattering of photons and surface-plasmon creation by photons at a rough metal surface. We have approximated the metal by an electron gas of uniform density which is bounded by a nearly plane surface at which the density falls abruptly to zero. Quantum perturbation theory is used to evaluate the probability of occurrence of the various processes at the assumed "weakly" rough surface.

I. INTRODUCTION

Collective electron polarization resonances in solids can be excited by photons and by energetic charged particles. These resonances may become manifest when photons having quantum energies in

the few eV range impinge on metal surfaces. At a rough surface photons may excite collective electron states which cannot be excited at a perfectly smooth surface. The smoothest metal surfaces which can be prepared by existing techniques have residual roughnesses of the order of 10 Å rms variation around the mean; even under these conditions photon–surface-plasmon coupling may be appreciable.

The importance of this rough surface absorption effect has become apparent through recent experimental work of Jasperson and Schnatterly,[1] Stanford et al.,[2] Dobberstein et al.,[3] Feuerbacher and Steinmann,[4] Beaglehole and Hunderi,[5] and more recently Endriz and Spicer.[6] It now appears that such absorption may affect markedly the values of the complex dielectric function inferred from reflectance measurements on metals and perhaps on other kinds of solids as well.

This paper gives a theoretical analysis of the effect of the collective surface mode upon the reflectance of a very thick metal specimen, in the approximation that the dielectric permittivity of the bulk metal is well approximated by that of a system of free electrons. Since the presence of surface roughness gives rise to diffuse scattering of an incident photon, we also analyze this phenomenon by the same method.

Fedders,[7] Ritchie and Wilems,[8] and Crowell and Ritchie[9] have proposed theories of the surface collective mode effect on optical reflectance of metals. The present approach includes the full transversality of the surface plasmon, neglecting hydrodynamic effects in the main. However, a brief approximate treatment of the effect of hydrodynamic dispersion on reflectance at frequencies corresponding to large surface-plasmon momenta is given in Sec. VI below. The theories of Fedders[7] and Ritchie and Wilems[8] both neglect the effect of retardation on the surface-plasmon field. Crowell and Ritchie[9] have included retardation but employed a form of perturbation theory which is equivalent to the classical field perturbation theory used by Stern[10] and Kretschmann and Raether[11] in treating the interaction of light with the radiative normal surface plasmon in a thin plane metal slab with rough surfaces. We argue below that the form of perturbation theory used in the present paper should be more accurate than that used by these workers.

Although we employ first-order time-dependent perturbation theory in this paper, we plan to extend the present approach to second order in a subsequent publication so as to be able to treat resonant diffuse scattering through the plasmon intermediate state. Experimental data bearing on this phenomenon have been obtained by Hunderi and Beaglehole[5] and by Stanford[2] using Ag metal foils.

A brief account of our work has appeared elsewhere.[12]

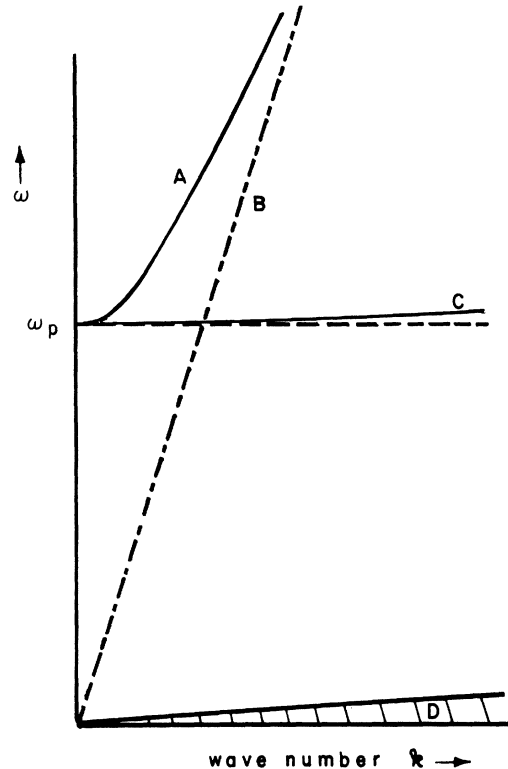wave number $\mathbf{k} \longrightarrow$

FIG. 1. Dispersion curves for the photon (curve A) and the plasmon (curve C) in an infinite homogeneous isotropic plasma system at the absolute zero of temperature. Curve B shows the dispersion curve $\omega = ck$ for photon *in vacuo*. Also shown schematically is the region D in the ω-k plane in which the excitation of single electron-hole pairs is energetically possible.

II. PLASMON FIELD AND RADIATION FIELD AT A SMOOTH SURFACE

It is well known that in an infinite homogeneous isotropic electron gas there is a clear and complete separation between longitudinal and transverse collective modes.[13] Figure 1 shows a schematic representation of the dispersive properties of these modes, together with an indication of the region in the ω-k plane in which single-particle interactions are important. The upper curve, whose equation is $\omega = (\omega_p^2 + c^2 k^2)^{1/2}$, might be called the plasma-shifted light line. It is interesting that when one couples the radiation field and the plasma in a very large system the plasmon dispersion curve is unaffected while the transverse field relation is strongly shifted from the vacuum relation $\omega = ck$. Here ω_p is the plasma frequency of the electron gas.

Suppose now that the plasma is bounded by an infinite smooth plane surface. As is well known, new modes appear as indicated in Fig. 2. A slow surface wave splits from the continuum and is asymptotic to the value $\omega = \omega_p/\sqrt{2}$ for large wave numbers
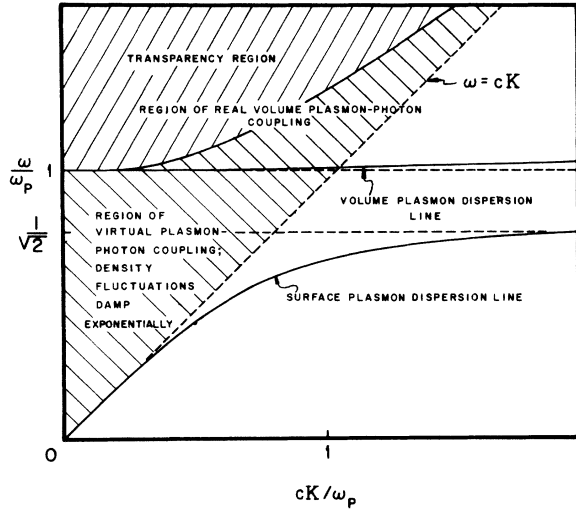
FIG. 2. Frequency–wave-number space appropriate to a semi-infinite plane-bounded electron gas. The wave vector $\vec{\kappa}$ is parallel with the bounding surface. The line labeled "volume-plasmon dispersion line" is sketched for the special case of a volume plasmon with zero momentum perpendicular to the surface. There is actually a continuum of possible $\omega - \kappa$ values lying above this line corresponding to various volume-plasmon momenta perpendicular to the surface; this continuum is indicated by the legend "region of real volume-plasmon–photon coupling." The surface-plasmon dispersion line is sketched asymptotic to the frequency $\omega = \omega_p/\sqrt{2}$, but increases above this value if hydrodynamic dispersion is allowed for.

in the case of the electron gas. This mode is a special case of the Sommerfeld-Zenneck wave much discussed in the literature of radio transmission theory in connection with the field of dipole antennas over a plane air-earth interface.[14] It has been studied by Stern[15] and others in the plasma case. Figure 2 shows the dispersion curve of the surface wave for the free-electron gas. The quantity κ is here the wave number of the surface plasmon parallel to the surface.

The presence of the surface means that momentum perpendicular to it is not a constant of the motion. The space eigenfunction of the photon in vacuum bounded by the plasma is strongly modified in the region below the line $\omega = (\omega_p^2 + c^2\kappa^2)^{1/2}$. The radiation field is damped exponentially into the plasma here. A standing wave representation for the photon is appropriate in this situation. In the region above this line the plasma is transparent to light in the neglect of absorptive processes and the appropriate spatial eigenfunctions for the photon field are incident plus reflected and transmitted waves.

The presence of the single surface modifies the spatial form of the volume-plasmon eigenfunction but does not change its dispersive characteristics. An interesting phenomenon which occurs for fre-

quencies $\omega > \omega_p$ is that of real photon–volume-plasmon coupling by virtue of the presence of the surface. This was apparently first studied in detail by Sauter[16] and Förstmann[17] for the case of plasmas at metallic densities. It appears to be a small effect at natural metal densities; it results in a decrease in reflectivity which is typically a small part of 1%[16–18] in the geometry of interest here.

III. HAMILTONIAN OF PLANE-BOUNDED ELECTRON GAS RADIATION FIELD SYSTEM

In Refs. 8 and 9 the dynamics of the system under consideration were described using the Bloch hydrodynamic equations together with Maxwell's equations. In the present paper where attenuation is focused primarily upon "optical" resonances in which the wavelengths of the important modes to not greatly exceed $\lambda_p \equiv 2\pi c/\omega_p$, the wavelength of a photon having the plasmon energy, it is sufficient to neglect hydrodynamic dispersion effects. Here we write Maxwell's equations in terms of the vector potential $\vec{A}$ as

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\vec{A}(\vec{r},\, t) = -\frac{4\pi}{c}\vec{j} + \nabla(\nabla\cdot\vec{A}),\tag{1}$$

$$\nabla\cdot\dot{\vec{A}} = 4\pi ec(n - n_0).\tag{2}$$

Here $\vec{j} = -en(\vec{r},\, t)\vec{v}(\vec{r},\, t)$ and $n(\vec{r},\, t)$ and $\vec{v}(\vec{r},\, t)$ are taken to be the electronic number density and velocity of the electron gas, respectively. $n_0(\vec{r})$ is the static density in the undisturbed electron gas. We work in the gauge $\phi = 0$, so that $\vec{E} = -(1/c)\dot{\vec{A}}$ and $\vec{H} = \nabla\times\vec{A}$. The equation of motion of the electrons in the free-electron gas is taken to be

$$\dot{\vec{v}} = (e/m^*c)\dot{\vec{A}}.\tag{3}$$

Integrating this equation with respect to time, setting the constant of integration equal to zero, defining a position-dependent "plasma frequency" by $\omega_p(\vec{r},\, t) = [4\pi n(\vec{r},\, t)e^2/m^*]^{1/2}$, and combining Eqs. (1) and (3), one finds

$$\left\{\nabla^2 - \frac{1}{c^2}\left[\frac{\partial^2}{\partial t^2} + \omega_p^2(\vec{r},\, t)\right]\right\}\vec{A}(\vec{r},\, t) = \nabla(\nabla\cdot\vec{A}),\tag{4}$$

$$\nabla\cdot\dot{\vec{A}} = 4\pi ec[n(\vec{r},\, t) - n_0(\vec{r})].\tag{5}$$

In the above, m^* may be taken as the effective mass of an electron in the system.

The energy residing in the fields plus the kinetic energy of the electron gas may be written

$$\mathcal{H} = (8\pi c^2)^{-1}\int d^3r\,[\dot{\vec{A}}^2 + c^2(\nabla\times\vec{A})^2]$$

$$+ \tfrac{1}{2}m\int d^3rn(\vec{r},\, t)\vec{v}^2(\vec{r},\, t).\tag{6}$$

Substituting from Eq. (3) above we find

$$\mathfrak{R} = (8\pi c^2)^{-1} \int d^3r \, [\dot{\vec{A}}^2 + \omega_p^2(\vec{r})\vec{A}^2 + c^2(\nabla \times \vec{A})^2] \, , \quad (7)$$

where the time-independent position-dependent plasma frequency $\omega_p^2(\vec{r}) = 4\pi n_0(\vec{r})e^2/m^*$ is employed in a linearized approach to the problem.

To make the model definite we may take $n_0(\vec{r}) = n_0\vartheta(z)$, where $\vartheta(z)$ is the unit step function. We thus assume the electron gas to be located in the region $z > 0$ and to have uniform density n_0 in that region and zero outside of it. We then seek normal mode solutions of the equations

$$\left\{ \nabla^2 - \frac{1}{c^2}\left[\frac{\partial^2}{\partial t^2} + \omega_p^2 \vartheta(z) \right] \right\} \vec{A} = 0 \quad (8a)$$

and

$$\nabla \cdot \vec{A} = 0 \quad (8b)$$

in the region $z \neq 0$, where the usual conditions of continuity of the tangential components of the fields across the plane $z = 0$ are to be satisfied.

To find characteristic solutions of the wave equation for the vector potential $\vec{A}(\vec{r}, t)$ given in Eqs. (8), one makes the standard ansatz

$$\vec{A}(\vec{r}, t) = \sum_{\vec{\kappa}} \vec{A}_{\vec{\kappa}}(z) N_{\vec{\kappa}}(t) e^{i\vec{\kappa}\cdot\vec{\rho}} \, ,$$

where $\vec{\rho} = \hat{x}x + \hat{y}y$ is a vector parallel to the x-y plane, $\vec{\kappa} = \hat{x}\kappa_x + \hat{y}\kappa_y$, and the eigenfrequency ω depends on both κ and the wave number of the vacuum field in the z direction. The time-dependent amplitude $N_{\vec{\kappa}}(t)$ is assumed to satisfy the oscillator equation $(d^2/dt^2 + \omega_\kappa^2)N_{\vec{\kappa}} = 0$. One finds

$$\left(\frac{d^2}{dz^2} - \nu^2 \right) \vec{A}_{\vec{\kappa}}^{(+)}(z) = 0 \, , \quad \left(\frac{d^2}{dz^2} + q^2 \right) \vec{A}_{\vec{\kappa}}^{(-)}(z) = 0 \, , \quad (9)$$

where $\nu^2 = \kappa^2 + (\omega_p^2 - \omega^2)/c^2$ and $q^2 = \omega^2/c^2 - \kappa^2$. We restrict attention here to the region of wave-number space for which $\nu^2 > 0$, i.e., to fields corresponding to propagating waves in the region $z < 0$ which are exponentially attenuated into the electron gas. The superscripts $+$ and $-$ refer to the regions $z > 0$ and $z < 0$, respectively.

A. s-Polarized Photons

We first consider photons polarized with $\vec{E}$ field perpendicular to the z axis (s polarization). Basic solutions of Eqs. (9) may be written

$$\vec{A}_{\vec{\kappa}}^{(+)}(z) = iA_{\vec{\kappa}q}^{(+)}(\hat{\kappa} \times \hat{z})e^{-\nu z} \, ,$$

$$\vec{A}_{\vec{\kappa}}^{(-)}(z) = i(\hat{\kappa} \times \hat{z})\{ A_{\vec{\kappa}q}^{c} \cos qz + A_{\vec{\kappa}q}^{s} \sin qz \} \, , \quad (10)$$

where $\hat{\kappa} = \vec{\kappa}/|\vec{\kappa}|$ is a unit vector in the direction of $\vec{\kappa}$. The three constants $A_{\vec{\kappa}q}^{(+)}$, $A_{\vec{\kappa}q}^{c}$, and $A_{\vec{\kappa}q}^{s}$ are to be determined by continuity requirements on the electromagnetic fields. The factor i has been included to account explicitly for the reality requirement

$\vec{A}_{\vec{\kappa}q} = \vec{A}_{-\vec{\kappa}q}^*$. If one now requires that the tangential components of $\vec{E}$ and $\vec{H}$ derived from $\vec{A}$ to be continuous across the plane $z = 0$ and that $\vec{\nabla} \cdot \vec{A} = 0$ everywhere except possibly at the plane $z = 0$, one finds

$$\vec{A}(\vec{r}, t) = \sum_{\vec{\kappa}} \int dq \left\{ i(\hat{\kappa} \times \hat{z})N_{\vec{\kappa}q}e^{i\vec{\kappa}\cdot\vec{\rho}} \right. \\ \left. \times \left[\vartheta(z)e^{-\nu z} + \vartheta(-z)\left(\cos qz - \frac{\nu}{q}\sin qz \right) \right] \right\} \, , \quad (11)$$

where the time-dependent amplitude $N_{\vec{\kappa}q}$ satisfies $(d^2/dt^2 + \omega_{\vec{\kappa}q}^2)N_{\vec{\kappa}q} = 0$ and where $\omega_{\vec{\kappa}q}^2 = c^2(\kappa^2 + q^2)$. It is fairly convenient here to use a mixed representation for the spatial variation of the vector potential; the wave number q characterizing the z variation of the eigenfunctions is taken to be a continuous variable while the components of $\vec{\kappa}$ are taken to be discrete, e.g., $\kappa_x = 2\pi n_x/L$ and $\kappa_y = 2\pi n_y/L$ where n_x and n_y are integers and the basic eigenfunction $e^{i\vec{\kappa}\cdot\vec{\rho}}$ satisfies periodic boundary conditions on the planes $x = \pm\frac{1}{2}L$ and $y = \pm\frac{1}{2}L$.

If one substitutes Eq. (11) into the expression for H_0 given in Eq. (7) and uses the orthogonality property of the basic eigenfunctions appearing in Eq. (11), one finds

$$\mathfrak{R}_0 = (L^2/16c^2)\sum_{\vec{\kappa}} \int dq(1 + \nu^2/q^2)(\dot{A}_{\vec{\kappa}q}\dot{A}_{\vec{\kappa}q}^* + \omega_{\vec{\kappa}q}^2 A_{\vec{\kappa}q}A_{\vec{\kappa}q}^*) \, . \quad (12)$$

Introducing the amplitudes $b_{\vec{\kappa}q}$ defined by $A_{\vec{\kappa}q} = \alpha_{\vec{\kappa}q} \times (b_{\vec{\kappa}q} + b_{-\vec{\kappa}q}^*)$ and $\dot{A}_{\vec{\kappa}q} = -i\omega_{\vec{\kappa}q}\alpha_{\vec{\kappa}q}(b_{\vec{\kappa}q} - b_{-\vec{\kappa}q}^*)$, one comes to the standard canonical form

$$\mathfrak{R}_0 = \sum_{\vec{\kappa}} \int dq \, \hbar\omega_{\vec{\kappa}q}b_{\vec{\kappa}q}^*b_{\vec{\kappa}q} \, ,$$

where $\alpha_{\vec{\kappa}q}$ are normalization constants. Since this equation is in canonical form, the fields may be quantized immediately by letting the $b_{\vec{\kappa}q}$ become photon annihilation operators satisfying the basic commutation relations $[b_{\vec{\kappa}q}, b_{\vec{\kappa}'q'}^\dagger] = \delta_{\vec{\kappa},\vec{\kappa}'}\delta(q - q')$. With this normalization the vector potential may be written in terms of these operators in the form

$$\hat{\vec{A}}_R^{(1)} = \sum_{\vec{\kappa}} \int dq(i\hat{\kappa} \times \hat{z})\left(\frac{4\hbar c^2\omega\mu^2}{\omega_p^2 L^2} \right)^{1/2} \\ \times \left[\vartheta(z)e^{-\nu z} + \vartheta(-z)\left(\cos qz - \frac{\nu}{q}\sin qz \right) \right] \\ \times e^{i\vec{\kappa}\cdot\vec{\rho}}(b_{\vec{\kappa}q1} + b_{-\vec{\kappa}q1}^\dagger) \, , \quad (13)$$

where the superscript (1) has been added to indicate s polarization, $\mu = cq/\omega$, and $\omega = c(\kappa^2 + q^2)^{1/2}$.

The integral over q covers the range from 0 to ω_p/c. A different analytical form for $\vec{A}_R$ must be used when $q > \omega_p/c$. This region corresponds, of course, to that in which the electron gas becomes transparent, in which case the appropriate spatial

eigenfunctions must describe fields transmitted into the electron gas as well as reflected from it. Since the region $\omega > \omega_p$ will not concern us here, we do not need to consider the form of $\hat{\vec{A}}$ appropriate to this region.

B. p-Polarized Photons

Similar considerations for photons which are polarized with $\vec{E}$ vector parallel to a plane containing the $\hat{z}$ axis and the vector $\vec{\kappa}$ yield

$$\hat{\vec{A}}_R^{(2)} = \sum_{\vec{\kappa}} \int dq (4\hbar c^2 \mu^2/L^2 \omega)^{1/2} \{(i\hat{\kappa} - \hat{z}\,\kappa/\nu)\cos\eta\, e^{-\nu z}\, \Im(z)$$

$$+ [i\hat{\kappa}\cos(qz+\eta) + (\hat{z}\vec{\kappa}/q)\sin(qz+\eta)]\Im(-z)\}$$

$$\times e^{i\vec{\kappa}\cdot\vec{\rho}}(b_{\vec{\kappa}q2} + b^\dagger_{-\vec{\kappa}q2}) \ , \quad (14)$$

where the superscript 2 has been used to indicate p polarization, $\cos\eta = \sigma/(\sigma^2 + \mu^2\epsilon^2)^{1/2}$, $\sin\eta = -\mu\epsilon/(\sigma^2 + \mu^2\epsilon^2)^{1/2}$, $\sigma = (1 - \epsilon - \mu^2)^{1/2}$, and $\epsilon = 1 - (\omega_p/\omega)^2$. It should be noted that the phase angle η may be taken to lie in the interval $0 \le \eta \le \frac{1}{2}\pi$, since ϵ is negative in the range of frequencies of interest here.

It may be shown that the current of photons of either polarization in the incident beam at large distances from the plane $z = 0$ which cross an area with unit normal $\hat{n}$ is given by $j = (c/2\pi L^2)$ $\times \hat{n} \cdot (\hat{\kappa}\sin\theta + \hat{z}\cos\theta)$, where $\mu = \cos\theta = cq/\omega$ and $\sin\theta = c\kappa/\omega$.

The operators $b_{\vec{\kappa}q\lambda}$ satisfy the commutation relations

$$[b_{\vec{\kappa}q\lambda}, b_{\vec{\kappa}',q',\lambda'}] = [b^\dagger_{\vec{\kappa},q,\lambda}, b^\dagger_{\vec{\kappa}',q',\lambda'}] = 0 \ ,$$

$$[b_{\vec{\kappa}q\lambda}, b^\dagger_{\vec{\kappa}',q',\lambda'}] = \delta^2_{\vec{\kappa},\vec{\kappa}'}\delta(q-q')\delta_{\lambda,\lambda'} \ .$$

C. Surface-Plasmon Field

In the present approximation, the vector potential operator corresponding to a wave bound to the surface is obtained following the general procedure described above. We find

$$\hat{\vec{A}}_S = \sum_{\vec{\kappa}} (4\pi\hbar c/L^2 p_\kappa)^{1/2}[(i\hat{\kappa} - \hat{z}\kappa/\nu)e^{-\nu z}\Im(z)$$

$$+ (i\hat{\kappa} + \hat{z}\,\kappa/\nu_0)e^{\nu_0 z}\Im(-z)]e^{i\vec{\kappa}\cdot\vec{\rho}}\,(b_{\vec{\kappa}} + b^\dagger_{-\vec{\kappa}}) \ , \quad (15)$$

where the $b_{\vec{\kappa}}$ again satisfy Boson commutation relations and commute with the $b_{\vec{\kappa}q\lambda}$. Here $p_\kappa = (\epsilon^4 - 1)/\epsilon^2$ $\times [-(\epsilon+1)]^{1/2}$, $\epsilon = 1 - (\omega_p/\omega_{\vec{\kappa}})^2$, and $\omega_{\vec{\kappa}}$ is the surface-plasmon eigenfrequency corresponding to a surface plasmon with wave number κ. The well-known eigenfrequency wave-number relation is $\kappa^2 = (\omega^2/c^2)\epsilon/(1+\epsilon)$ which may be solved explicitly for $\omega_{\vec{\kappa}}$ in the electron gas case. One finds $\omega_{\vec{\kappa}}^2 = \frac{1}{2}\omega_p^2 + c^2\kappa^2$ $- [\frac{1}{4}\omega_p^4 + c^4\kappa^4]^{1/2}$ which seems to have been given first by Stern[15] for the electron gas. In Eq. (15) $\nu^2 = \kappa^2 - (\omega_{\vec{\kappa}}^2 - \omega_p^2)/c^2$ and $\nu_0^2 = \kappa^2 - \omega_{\vec{\kappa}}^2/c^2$.

It should be emphasized that the operators $b_{\vec{\kappa}}$ and

$b_{\vec{\kappa}q\lambda}$ correspond to modes of the system which are orthogonal to one another; thus the photon and the surface plasmon (SP) on the perfectly smooth, plane-bounded electron gas do not couple with one another not only because momentum-energy conditions cannot be satisfied but also because of the fact of orthogonality.

IV. INTERACTION HAMILTONIAN DUE TO SURFACE ROUGHNESS

To introduce the essential feature of surface roughness into our model, we follow Fedders[7] in making the basic assumption that the actual surface may be described by the single-valued function $z = \zeta(x, y)$ such that for $z > \zeta$ the system consists of an electron gas with constant density n_0 and that the region $z < \zeta$ is empty. The function ζ may be described stochastically as in the present connection, or alternatively, may be a periodic function of position, i.e., a metal diffraction grating. For convenience, we may take $\langle\zeta\rangle = 0$.

In this case we may write the system Hamiltonian as

$$\mathcal{K} = (8\pi c^2)^{-1}\int d^3r[\dot{\vec{A}}^2 + \Im(z - \zeta(x, y))\omega_p^2\vec{A}^2 + c^2(\nabla\times\vec{A})^2] \ . \quad (16)$$

We transform coordinates[7] to the nonorthogonal system $u_1 = x$, $u_2 = y$, $u_3 = z - \zeta(x, y)$. Expressing the factor $\vec{A} = \hat{e}_1 A_1 + \hat{e}_2 A_2 + \hat{e}_3 A_3$ in terms of the unit vectors $(\hat{e}_1, \hat{e}_2, \hat{e}_3)$ tangential to the coordinate curves in the (u_1, u_2, u_3) system, we may write

$$\mathcal{K} \doteq \mathcal{K}_0 + \mathcal{K}_1 + \mathcal{K}_2 \ , \quad (17)$$

where

$$\mathcal{K}_0 = (8\pi c^2)^{-1}\int d^3u \sum_{i=1}^{3} [\dot{A}_i^2 + \Im(u_3)\omega_p^2 A_i^2 + c^2 H_i^2] \quad (18)$$

and $H_i = \partial A_k/\partial u_j - \partial A_j/\partial u_k$ with cyclic permutations of the coordinate indices. This Hamiltonian is exactly that which would be appropriate if the system (u_1, u_2, u_3) consisted of orthogonal Cartesian coordinates, i.e., no evidence of nonorthogonality is displayed in this portion of the total Hamiltonian. The Hamiltonian $\mathcal{K}_1$ is defined to contain only terms linear in $\zeta(u_1, u_2)$, viz.,

$$\mathcal{K}_1 = \frac{1}{4\pi c^2}\int d^3u \left\{ \dot{D}\dot{A}_3 + \Im(u_3)\omega_p^2 DA_3 \right.$$

$$\left. -c^2\left[D\left(\frac{\partial H_1}{\partial u_2} - \frac{\partial H_2}{\partial u_1}\right) + \left(\frac{\partial}{\partial u_3}F\right)H_3 - G\frac{\partial A_3}{\partial u_3}\right]\right\} \ , \quad (19)$$

where

$$D = \frac{\partial\zeta}{\partial u_1}A_1 + \frac{\partial\zeta}{\partial u_2}A_2, \quad F = \frac{\partial\zeta}{\partial u_1}A_2 - \frac{\partial\zeta}{\partial u_2}A_1,$$

$$G = \frac{\partial \zeta}{\partial u_1} H_2 - \frac{\partial \zeta}{\partial u_2} H_1 \; .$$

The Hamiltonian $\mathcal{H}_2$ contains all terms involving ζ to higher order than the first. It will not be written out here since we are interested primarily in surfaces which are "weakly" rough.

In the present paper we will treat $\mathcal{H}_1$ as a perturbation Hamiltonian, the expectation value of which is in some sense small compared with that of $\mathcal{H}_0$.

V. FIRST-ORDER PROCESSES

We now proceed to describe the interaction of a photon, incident upon a nonplanar interface between an electron gas and vacuum, with the surface plasmon and with photons having different momenta parallel with the average surface. This is done in the context of first-order perturbation theory, treating $\mathcal{H}_1$ as a small quantity and $\mathcal{H}_2$ as negligible.

We employ normal-mode expansions for the photon fields, a typical member of which consists of an incident wave with momentum $\hbar \vec{\kappa}$ parallel with the surface plus a reflected wave with the same momentum, accompanied by a field which is exponentially attenuated into the metal. Although the final state, in the case of elastic diffuse scattering on the rough surface, also consists of both "incident" and "reflected" waves, it may be shown, in the framework of time-dependent perturbation theory, that only that part of the wave which describes photons traveling away from the surface (the "reflected" portion) makes a contribution to the real photon field at large distances from the surface.[19]

Since the "roughness parameter" ζ is contained entirely in $\mathcal{H}_1$ and $\mathcal{H}_2$, we may treat the zero-order fields, which are eigenfunctions of $\mathcal{H}_0$, as expandable in terms of the orthogonal modes described by Eqs. (12)–(14). The vector potential operators $\vec{A}_S$ and $\vec{A}_R^{(\lambda)}$ may now be considered to depend upon the coordinates (u_1, u_2, u_3) rather than (x, y, z) so that the zero-order fields correspond to waves propagating along the actual rough surface $z = \zeta(x, y)$ $\equiv \zeta(\vec{\rho})$. The coupling between these waves arises entirely through the coordinate transformation terms contained in $\mathcal{H}_1$ and $\mathcal{H}_2$. It seems that a perturbation theory based upon this approach should give better results than one which begins with fields propagating on a smooth "fictitious" surface which is located somewhere between the extreme excursions of the actual nonplane surface. Lippman[20] has criticized the Rayleigh[21]-Fano[22] theory of diffraction grating anomalies on the basis that their zero-order fields, which are essentially tied to a fictitious plane surface, cannot describe correctly the real fields in the neighborhood of the grooves. This objection does not apply to the scheme used here. The basic conceptual indeterminacy in the

location of the fictitious smooth surface relative to the real rough surface could conceivably be removed by appealing to a variational principle to fix its location. Some work along these lines has been carried out[23] but requires a great deal more analytical labor than the present theory, in which the calculation begins with (approximate) fields which are associated with the actual surface.

The effect on the eigenvalues and eigenfunctions of a change in a bounding surface has been considered by many different workers in connection with Schrödinger's equation and the wave equation in acoustics and electromagnetic theory.[24]

A. Photon-Plasmon Coupling

We suppose that a photon is incident on a vacuum electron gas interface in a direction normal to the mean surface plane. We apply first-order perturbation theory to determine the transition rate from an initial state $b_{\vec{\kappa}_0 q_0 \lambda}^\dagger | 0 \rangle$ to a final state $b_{\vec{\kappa}}^\dagger | 0 \rangle$, where the state vector $| 0 \rangle$ represents the photon–surface-plasmon vacuum state $(b_{\vec{\kappa} q \lambda} | 0 \rangle = b_{\vec{\kappa}} | 0 \rangle = 0$ for all $\vec{\kappa}$, q, and λ). Since we assume normal incidence, we take $\vec{\kappa}_0 \to 0$.

The interaction Hamiltonian $\mathcal{H}_1$ simplifies considerably in this case. We may take the incident photon to be polarized with its $\vec{E}$ field entirely in the $\hat{e}_1$ direction. Since we are interested in interactions only on the energy shell, we may write for this special case

$$\mathcal{H}_1 = -\frac{1}{4\pi c^2} \int d^3 u \, \zeta(u_1, u_2) \left(2\omega^2 \hat{A}_{R1}^{(2)} \frac{\partial}{\partial u_1} \hat{A}_{S3} \right.$$

$$\left. + c^2 \hat{H}_{R2}^{(2)} \frac{\partial^2}{\partial u_1 \partial u_3} \hat{A}_{S3} \right) \; , \quad (20)$$

where ω is the (common) frequency of the photon and the plasmon field and where an integration by parts with respect to the u_1 variable has been carried out, assuming that $\lim \zeta = 0$ as $|u_1| \to \infty$.

The transition rate γ for the photon–surface-plasmon conversion process is given by

$$\gamma = \sum_{\vec{\kappa}} (2\pi/\hbar) \, | \langle 0 | b_{\vec{\kappa}} \mathcal{H}_1 b_{\vec{\kappa}_0 q_0}^\dagger {}_2 | 0 \rangle |^2 \delta(\hbar \omega_{\vec{\kappa}_0 q_0} - \hbar \omega_{\vec{\kappa}}) \quad (21)$$

according to the Fermi Golden Rule. The probability P_s for the radiation to surface-plasmon conversion process is equal to λ divided by $c/2\pi$, the rate at which photons strike the entire surface of area L^2. Converting the sum over final momenta $\vec{\kappa}$ to an integral in the limit $L \to \infty [\sum_{\vec{\kappa}} \to (L/2\pi)^2 \int d^2\kappa]$ and converting to an integral over frequency, i.e.,

$$\int d^2 \kappa = \int_0^{2\pi} d\phi_f \int_0^\infty \kappa \frac{d\kappa}{d\omega_{\vec{\kappa}}} d\omega_{\vec{\kappa}} \; ,$$

one finds after some algebra

$$P_S = \left(\frac{\omega_p}{c}\right)^4 F(\alpha) \frac{1}{\pi} \int_0^{2\pi} \cos^2\phi_f \, d\phi_f \frac{1}{L^2} |\zeta_{\vec{\kappa}}|^2 \, , \quad (22)$$

where

$$\alpha = \frac{\omega}{\omega_p} \, , \quad F(\alpha) = \frac{\alpha^5(1-\alpha^2)^2}{(1-2\alpha^2)^{5/2}} \left[1 + 2\left(\frac{1-2\alpha^2}{1-\alpha^2}\right)^{1/2}\right]^2 \, ,$$

and

$$|\vec{\kappa}| = \frac{\alpha\omega_p}{c}\left(\frac{1-\alpha^2}{1-2\alpha^2}\right)^{1/2} \, ,$$

and where

$$\zeta_{\vec{\kappa}} = \int du_1 \int du_2 \, e^{i\vec{\kappa}\cdot\vec{p}} \zeta(\vec{\rho})$$

is the Fourier transform of the function $\zeta(u_1, u_2)$ $= \zeta(\vec{\rho})$, which describes the height of the surface at the point $(u_1, u_2) = (x, y)$. The angle $\phi_f = \cos^{-1}(\hat{\kappa}\cdot\hat{e}_1)$ is the angle between the plasmon wave vector $\vec{\kappa}$ and $\hat{e}_1$ coordinate axis which we have taken to be parallel with the $\vec{E}$ field of the incident photon. We have neglected the finite lifetime of the surface-plasmon state in obtaining this expression.

For comparison with experimental data on metal surfaces it is reasonable to assume that a given surface structure is describable by some sort of stochastic process and that one should average Eq. (22) over an ensemble of statistically independent surfaces; as is usual, one may assume that this ensemble average does not differ appreciably from the spatial average over a single surface. For simplicity we assume that after averaging, the probability P_s depends only upon the magnitude of $\vec{\kappa}$, not upon its direction. If we neglect the possibility that the surface plasmon generated may decay into a photon, which is certainly justified if $\langle\zeta^2\rangle$ is small enough, and set $\langle P_s\rangle$, the ensemble average of P_s, equal to $\Delta R_s(\omega)$, the decrease in reflectance of the rough surface for photons of energy $\hbar\omega$, we have

$$\Delta R_s(\omega) = \delta^2\left(\frac{\omega_p}{c}\right)^4 F(\alpha) g\left(\frac{\alpha\omega_p}{c}\left[\frac{1-\alpha^2}{1-2\alpha^2}\right]^{1/2}\right) \, . \quad (23)$$

Note that $\Delta R_s = 0$ for $\alpha^2 > \frac{1}{2}$, in which frequency range the SP does not exist. The replacement $L^{-2}\langle|\zeta_{\vec{\kappa}}|^2\rangle = \delta^2 g(\kappa)$ has been made in obtaining Eq. (23). The mean-square surface height variation $\langle\zeta^2\rangle \equiv \delta^2$, while $g(\kappa)$ may be thought of as a *surface scattering factor*, the two-dimensional analog of the x-ray scattering factor for matter. The argument of g in Eq. (23) is just the wave number of a surface plasmon of frequency ω.

We may compare the result for $\Delta R_s(\omega)$ from Eq. (23) above with the expression for $\Delta R(\omega)$ obtained by Crowell and Ritchie[9] in their Eq. (24) using a different form of perturbation theory but for the same dissipationless electron gas model used here. The present result is larger than that of Ref. (9) by the factor

$$\left[1 + 2\left(\frac{1-2\alpha^2}{1-\alpha^2}\right)^{1/2}\right]^2$$

and should be more accurate for the reasons advanced above. Note that the two different results coincide exactly at $\alpha^2 = \frac{1}{2}$ although the present formula may predict appreciably larger reflectance decreases at lower frequencies.

We may include line broadening effects by using the standard quantum-mechanical theory of final-state damping. We may use the approximation

$$\Delta R_s(\omega) = \frac{\delta^2}{2\pi}\left(\frac{\omega_p}{c}\right)^4 F(\alpha_{\vec{\kappa}}) \int_0^\infty d\omega_{\vec{\kappa}} \frac{\gamma_{\vec{\kappa}}}{(\omega - \omega_{\vec{\kappa}})^2 + (\frac{1}{2}\gamma_{\vec{\kappa}})^2}$$

$$\times g\left(\frac{\alpha_{\vec{\kappa}}\omega_p}{c}\left[\frac{1-\alpha^2}{1-2\alpha^2}\right]^{1/2}\right) \, , \quad (24)$$

where $\alpha_\kappa = \omega_{\vec{\kappa}}/\omega_p$ and γ_κ is the total damping rate of an SP with wave number κ. We may take

$$\gamma = \frac{\omega_p \alpha \epsilon_2}{1 + (1 - 1/\alpha^2)^2} \, ,$$

where it is assumed that the complex dielectric permittivity of the electron gas may be written $\epsilon(\omega)$ $= 1 - (\omega_p/\omega)^2 + i\epsilon_2(\omega)$, where $\epsilon_2 \ll |\epsilon_1|$, and $\epsilon_2(\omega)$ may be taken from experimental data on the metal in question. The actual damping rate of the SP is expected to be larger than that obtained using the expression for $\gamma_{\vec{\kappa}}$ suggested above, which assumes that a surface plasmon is damped at the same rate in a metal as a photon of the same frequency. Additional damping will occur due to radiative coupling through, and scattering on, the surface structure and also because the plasmon may have considerably shorter wavelength than a photon of the same frequency and hence may excite nonvertical interband transitions in the metal (referred to the reduced zone scheme).

We have given elsewhere[12] formulas equivalent to Eqs. (23) and (24) above for the case of a general dielectric medium characterized by the dielectric function $\epsilon(\omega)$.

B. Diffuse Scattering—s-Polarized Photons

Diffuse scattering from a rough surface removes photons from the specularly reflected beam. The reflectance decrease due to this process adds to that due to photon-SP conversion in an experimental situation unless special care is used to collect these photons. It is thus desirable to evaluate theoretically the probability of diffuse scatter.

We suppose again that a single photon state $b^\dagger_{\vec{\kappa}_0 q_0 2}|0\rangle$ is prepared initially. We take $\vec{\kappa}_0$ parallel with the $\hat{e}_1$ direction and let $|\vec{\kappa}_0| \to 0$ to correspond to normal incidence. We calculate the probability of exciting a photon polarized with its $\vec{E}$ vector perpendicular to the plane of observation by first-order

perturbation theory using the form

$$\mathcal{3C}_1^{(21)} = -\frac{1}{4\pi c^2} \int d^3u \; \zeta(u_1, u_2)\left(2\omega^2 \hat{A}_{R1}^{(2)} \frac{\partial}{\partial u_1} \hat{A}_{R3}^{(1)}\right.$$

$$\left. + c^2 \hat{H}_{R2}^{(2)} \frac{\partial^2}{\partial u_1 \partial u_3} \hat{A}_{R3}^{(1)}\right) \quad (25)$$

appropriate to the assumed initial state, again considering transitions to states on the energy shell. The total transition probability

$$P^s = (2\pi/c)\sum_{\vec{\kappa}} \int dq (2\pi/\hbar)\left|\langle 0 \left| b_{\vec{\kappa}q1} \mathcal{3C}_1^{(21)} b_{\vec{\kappa}_0 q_0}^\dagger \right| 0\rangle\right|^2$$

$$\times \delta(\hbar\omega_{\vec{\kappa}_0 q_0} - \hbar\omega_{\vec{\kappa}q}^{-}) \quad (26)$$

for scatter into all possible s-polarized photon states may be converted into a differential angular probability distribution by letting the sum over $\vec{\kappa}$ go to an integral as $L \to \infty$ and then transforming from $(\vec{\kappa}, q)$ to (ω, θ, ϕ) variables, where $\cos\theta = cq/\omega$. Thus $\int d^2\kappa \int dq = \int d\phi \int d(\cos\theta) \int d\omega (\omega^2/c^3)$, where we abbreviate $\omega = \omega_{\vec{\kappa}q}$ and ϕ is the azimuthal angle relative to the plane containing $\hat{e}_1$ and $\hat{e}_3$. The integration over ω may be done exactly; defining the infinitesimal solid angle $d\Omega = d\phi\, d(\cos\theta)$, we find

$$\frac{dP^s}{d\Omega} = \frac{\delta^2}{\pi^2}\left(\frac{\omega}{c}\right)^4 \cos^2\theta \sin^2\phi\, g\left(\frac{\omega}{c}\sin\theta\right) \quad (27)$$

after ensemble averaging as above. The angle θ may be interpreted as the spherical polar angle between the outward normal to the electron gas surface and the direction of observation (see Fig. 3). Since the azimuthal angle ϕ is referred to the direction of polarization of the normally incident photon, we may obtain $\langle dP^s/d\Omega\rangle_\phi$, the differential probability for diffuse scattering of initially unpolarized photons, by averaging this expression over all ϕ; thus

$$\left\langle\frac{dP^s}{d\Omega}\right\rangle_\phi = \frac{1}{2}\frac{dP^s}{d\Omega} \; .$$

This quantity may be compared with results of the scalar scattering theory of Davies[25] for the total yield of photons of both polarizations, assuming initially unpolarized radiation. Although he has taken a Gaussian autocorrelation function to describe surface roughness, his result is equivalent to twice the present result for $\langle dP^s/d\Omega\rangle_\phi = \frac{1}{2}dP^s/d\Omega$ in the region of small θ. His formula is most accurate for small θ because of approximations made in the mathematical treatment. He treats both polarization states in the scattered photon field on the same basis and finds equal contributions to each. As will be seen below, the present theory predicts that the p-polarization yield should have quite a different character from that displayed in Eq. (27).

It is interesting that the λ^{-4} factor in Eq. (27) is reminiscent of the Rayleigh formula for the scattering of light on polarizable spheres of radius small compared with the wavelength of the light.

C. Diffuse Scattering—p-Polarized Photons

The initial state is represented by the state vector $b_{\vec{\kappa}_0 q_0 2}^\dagger |0\rangle$ as before and transitions to final states represented by $b_{\vec{\kappa}q2}^\dagger |0\rangle$ corresponding to photons polarized with the electric field vector parallel with the plane of observation are considered. The interaction Hamiltonian due to surface roughness may be written

$$\mathcal{3C}_1^{(22)} = -\frac{1}{4\pi c^2} \int d^3u \; \zeta(u_1, u_2)\left(2\omega^2 \hat{A}_{R1}^{(2)} \frac{\partial}{\partial u_1} \hat{A}_{R3}^{(2)}\right.$$

$$\left. + c^2 \hat{H}_{R2}^{(2)} \frac{\partial^2}{\partial u_1 \partial u_3} \hat{A}_{R3}^{(2)}\right)$$

for this situation. As above, we calculate the transition probability between these states by Fermi Golden Rule; converting to a differential angular distribution, we find for normal incidence

$$\frac{dP^p}{d\Omega} = \frac{\delta^2}{\pi^2}\left(\frac{\omega}{c}\right)^4 \cos^2\theta \cos^2\phi\left(\frac{\sin^2\theta - \epsilon}{\sin^2\theta - \epsilon\cos^2\theta}\right)$$

$$\times \left(1 + \frac{2(-\epsilon)^{1/2}}{(\sin^2\theta - \epsilon)^{1/2}}\right)^2 g\left(\frac{\omega}{c}\sin\theta\right), \quad (28)$$

where $\epsilon = 1 - (\omega_p/\omega)^2$. If we wish to describe unpolarized incident radiation, we average over ϕ, obtaining a factor of $\frac{1}{2}$ in place of the $\cos^2\phi$ factor.

This result does not reduce to Davies's formula (or one-half of it) even in the limit $\omega \to 0$ where his assumption that the surface is perfectly conducting may be expected to be most accurate. The present
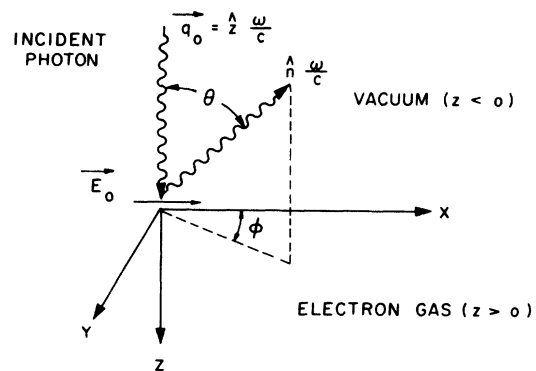

FIG. 3. Geometry of diffuse scattering. The incident photon is taken to have propagation vector parallel with the z axis and to be polarized with electric vector $\vec{E}_0$ parallel with the $+x$ direction. The scattered photon is taken to have propagation vector in the direction of the unit vector $\hat{n}$ which makes polar angle θ with respect to the $-z$ direction and azimuthal angle ϕ measured from the $\hat{x}$-$\hat{z}$ plane. The scattered photon may be either s or p polarized. The average surface coincides with the x-y plane.
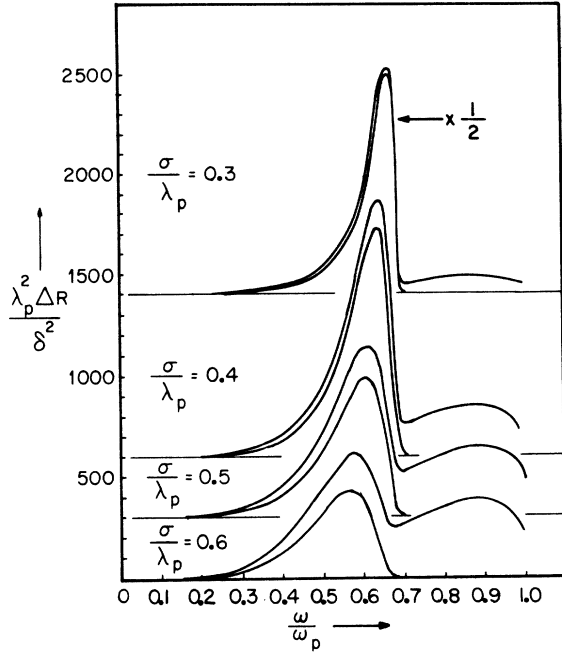
FIG. 4. Specular reflectance decrease as a function of frequency calculated for a Gaussian correlation function assuming various correlation lengths. The upper curve in each figure shows $\Delta R_T(\omega)$, while the lower curve gives $\Delta R_s(\omega)$. To save space, the curves corresponding to $\sigma/\lambda_p = 0.3$, 0.4, and 0.5 have been displaced vertically upward. For example, the zero of ΔR is measured from $(\lambda_p/\sigma)^2 \Delta R = 1400$ for the case $\sigma/\lambda_p = 0.3$.

result predicts considerably larger scattering, i.e., nine times larger for θ close to zero and even more as $\theta \to \frac{1}{2}\pi$. We suggest that our results should be more accurate than those obtained from the scalar scattering theory of Davies since we take specific account of the character of the p-polarized photon field in our treatment, while in the scalar theory no distinction between s and p photons is made.

Equation (28) bears an interesting similarity to the formula for the yield of transition radiation photons from a lossless semi-infinite electron gas bombarded by a swift charged particle.[26] Both formulas display a "near-resonance," i.e., both denominators vanish when $\theta \to 0$ and $\omega \to \omega_p$. Dissipation effects, of course, prevent real photon yields from becoming infinite in this limit. It is not surprising that this similarity exists; a fast charged particle induces radiation because polarization currents flow in response to the particle motion, while photon scattering occurs on a rough surface because currents flow in response to the field of the incident photon. Since these currents are associated with flow along a wavy surface and constitute an accelerated charge distribution, they may radiate also.

The Davies formula for the total decrease in the

specularly reflected beam takes on quite a simple form if the Gaussian autocorrelation function is used. In our way of doing things the total decrease in the specularly reflected beam due to diffuse elastic scatter *plus* surface-plasmon generation may be written

$$P_T(\omega) = 1 - e^{-\Delta R_T(\omega)},$$

where

$$\Delta R_T(\omega) = \int d\Omega \left(\frac{dP^s}{d\Omega} + \frac{dP^p}{d\Omega} \right) + \Delta R_S(\omega) \qquad (29)$$

for polarized normally incident photons. For the case of unpolarized incident photons we need only use $\langle dP^{(\lambda)}/d\Omega \rangle_{\phi}$ rather than $dP^{(\lambda)}/d\Omega$ in Eq. (29). The exponential dependence of $P_T(\omega)$ follows from the fact that the initial state is depleted due to transitions to final states. The present result for $P_T(\omega)$, as written, can be considered to satisfy unitarity requirements, while the Davies results do not appear to, in general.

The value of the function $\Delta R_T(\omega)$ clearly depends strongly upon the function $g(\kappa)$ appropriate to a given surface. To give some idea of how this function may look, we have plotted $(\delta/\lambda_p)^{-2} \Delta R_T(\omega)$ and $(\delta/\lambda_p)^{-2} \Delta R_S(\omega)$ from Eqs. (24) and (29), neglecting line broadening of the SP state and assuming a Gaussian autocorrelation function, i.e., $g(\kappa) = \pi\sigma^2 e^{-(\sigma\kappa/2)^2}$ for various values of the ratio σ/λ_p in Fig. 4.

VI. HYDRODYNAMIC EFFECTS

We wish to obtain an approximate result for the decrease in reflectance due to SP generation in the region of large plasmon momenta, where plasma dispersion may be important, possibly giving rise to photon-plasmon coupling at frequencies greater than $\omega_p/\sqrt{2}$, the nominal SP eigenfrequency. We assume that in this region electromagnetic retardation may be neglected, that dispersion is linear in κ, i.e.,

$$\omega_{\bar{\kappa}} \sim \omega_p/\sqrt{2} + (\tfrac{3}{20})^{1/2} v_F \kappa, \qquad (30)$$

where v_F is the Fermi speed in the electron gas, and that the SP field may be described by Eqs. (45) and (46) of Ref. 8. In this regime we may write from this same reference

$$\mathcal{K}_1 = -(en_0/c) \int d^3r\, \vartheta\,(z - \zeta(x, y))\hat{A}_R^{(2)} \cdot \nabla\hat{\Psi}_1, \qquad (31)$$

where $\hat{\Psi}_1$ is the velocity potential operator of the SP field. $\hat{A}$ is the vector potential operator for the photon field. Transforming coordinates as above, we have for p-polarized photons

$$\mathcal{K}_1 = -\frac{en_0}{c} \int d^3u\, \vartheta(u_3)\zeta(u_1, u_2)\hat{A}_R^{(2)} \frac{\partial^2}{\partial u_1 \partial u_3} \hat{\Psi}_1, \qquad (32)$$

where we use the fact that $\hat{A}_R^{(2)}$ does not depend upon

u_1 for the case of normally incident photons.

After a little calculation we find, assuming a Gaussian autocorrelation function,

$$\Delta R_s = \frac{\delta^2 \omega_s \omega}{\pi c \beta} \exp\left[-\left(\frac{\sigma}{\beta}(\omega - \omega_s)\right)^2\right] \qquad (33)$$

and $\Delta R_s(\omega) = 0$ when $\omega < \omega_s$ in this approximation. In this equation $\beta^2 = \frac{3}{5} v_F^2$, $\omega_s = \omega_p/\sqrt{2}$, and σ is the correlation length. This result is valid for normally incident photons. If we use parameters appropriate to Al metal and take $\delta = 18$ Å and $\sigma = 330$ Å to use figures which seem representative of experimentally determined values, [27] we find

$$\Delta R_s(\omega) \simeq 1.384\, e^{-32(E-E_s)^2} , \qquad (34)$$

where $E = \hbar \omega$ is in eV. This expression clearly decreases extremely rapidly as $E - E_s$ increases. The model used is inaccurate in that it predicts $\Delta R_s = 0$ for $E < E_s$ and $\Delta R_s(E) > 1$ when $E = E_s$; however, we find that even with hydrodynamic dispersion present, so that ω may be greater than ω_s, we do not obtain an appreciable spread in the reflectance decrease into the region $\omega > \omega_s$. Since hydrodynamic dispersion has recently been predicted[28] to be weaker than that given in Eq. (30), we may expect such spreading to be even less than that given in Eq. (34).

Experimental work by Endriz[27] indicates that the surface-plasmon eigenfrequency in the large κ limit is somewhat larger for a rough surface than for a smooth surface. A roughness-induced surface-plasmon energy shift may be calculated within the framework described in this paper. Preliminary results which we have obtained indicate that this shift is in reasonable agreement with that inferred by Endriz from his data. An account of this work will be published elsewhere.

VII. SUMMARY

We have presented theoretical results for the interaction probability of a photon with a "weakly" rough surface, including the possibility of diffuse scattering as well as surface-plasmon creation at the surface. The results are appropriate to a free-electron gas but should be useful in assessing the magnitude of the effect for real metals.

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