$$2E = E_1(1-x) + E_2(1+x)\ , \qquad \text{(D5)}$$

where

$$T_0(x) = 1\ , \quad T_1(x) = x\ ,$$
$$T_n(x) = 2xT_{n-1}(x) - T_{n-2}(x)\ , \qquad \text{(D6)}$$
$$R_n(E) = T_n(x)\ .$$

The $\vec{k}$-space transformation $U^{(2)}$ is obtained in a very similar manner using the summation orthogonality of the nine lowest-order cubic harmonics over any angular mesh having cubic symmetry. We specialize to $M=9$ letting $M'=12$ where $\vec{\Delta}_0 = \vec{0}$ and the remaining $\vec{\Delta}$'s are in the 12 various [110] directions. $U^{(2)}_{mj}$ is given by

$$U^{(2)}_{mj} = N_m^{-1}[P_m(\vec{\Delta}_j) - \delta_{j0}]\ , \quad m > 0 \qquad \text{(D7)}$$

$$N_m = \sum_{j=1}^{12} P_m^2(\vec{\Delta}_j)\ , \qquad \text{(D8)}$$

$$U^{(2)}_{0j} = \delta_{j0}\ , \qquad \text{(D9)}$$

where $P_0(\vec{r}) = 1$ and $P_m(\vec{r})$ for $1 \le m \le 9$ are x, y, x, yz, xz, xy, $x^2 - y^2$, $x^2 + y^2 - 3z^2$, and $x^2 + y^2 + z^2$.

---

[*] Based in part on work sponsored by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under Contract No. F44620-70-0089.

[1] A. R. Williams, J. F. Janak, and V. L. Moruzzi, J. Phys. Paris (to be published).

[2] J. Treusch, *Computational Solid State Physics*, edited by F. Herman, N. W. Dalton, and T. R. Koehler (Plenum, New York, 1972).

[3] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. <u>152</u>, 505 (1966); F. M. Mueller, *ibid.* <u>153</u>, 659 (1967).

[4] J. Korringa, Physica <u>13</u>, 392 (1946); W. Kohn and N. Rostoker, Phys. Rev. <u>94</u>, 1111 (1954).

[5] J. Ziman, Proc. Phys. Soc. (London) <u>86</u>, 337 (1965).

[6] P. O. Löwdin, J. Math. Phys. <u>6</u>, 1341 (1965); J. Chem. Phys. <u>43</u>, S175 (1965).

[7] O. K. Andersen, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971); O. K. Andersen and R. V. Kasowski, Phys. Rev. B <u>4</u>, 1064 (1971).

[8] N. W. Dalton, in Ref. 7.

[9] G. A. Burdick, Phys. Rev. <u>129</u>, 138 (1963).

[10] J. Keller, J. Phys. C <u>4</u>, L85 (1971); K. H. Johnson and F. C. Smith, Jr., in Ref. 7.

[11] V. Heine, Phys. Rev. <u>153</u>, 673 (1967).

[12] F. S. Ham and B. Segall, Phys. Rev. <u>124</u>, 1786 (1961).

[13] H. L. Davis, in Ref. 7.

[14] C. W. Clenshaw, E. T. Goodwin, D. W. Martin, G. F. Miller, F. W. J. Olver, and J. H. Wilkinson, *Modern Computing Methods* (Philosophical Library, New York, 1961).

PHYSICAL REVIEW B VOLUME 6, NUMBER 12 15 DECEMBER 1972

Electron Scattering from Surface Excitations*

S. Q. Wang and G. D. Mahan
Institute of Theoretical Science and Department of Physics,
University of Oregon, Eugene, Oregon 97403

(Received 19 January 1972)

Surface modes play an important role in a solid's response to external disturbances. A charged particle on approaching or leaving the surface may suffer inelastic scattering owing to its coupling with these modes. The scattering rate is calculated in the Born approximation for two instances: (i) in metals, where the surface modes are plasma oscillations and (ii) in dielectrics, with optical surface phonons. For electrons in a parabolic band with energy of the order of a few electron volts, it is found that on traversing the sample, the probability of scattering is of order 1. Furthermore, this probability is highly anisotropic. These findings strongly suggest that this scattering effect should be incorporated in the analysis of energy or spatial distribution of charged-particle probes, at least in the low-energy regime.

I. INTRODUCTION

There has been considerable interest in the spectra of electrons in photoemission studies.[1] The experiments show that some of the electrons leave the surface without apparent scattering, and some appear to be scattered.[2] This paper reports theoretical calculations of the scattering rate of electrons as they pass through surfaces. The inelastic scattering rate is calculated for the electron creating surface plasmons in a metal, and also surface optical phonons in a polar insulator.

There have been a number of recent papers on the scattering rate of electrons as they pass through surfaces.[3-5] Calculations have been done for exciting both surface plasmons and surface phonons. Most of these other calculations have assumed that the electron is sufficiently energetic that it does not change its direction or energy appreciably upon scattering. With this approximation, or assumption, the problem may be solved in an elementary way. The approximation is not valid for low-energy electrons.

In a typical photoemission experiment the electron energy is of the order 10 eV or less. After the emission or absorption of one quantum of surface excitation (energy $\lesssim 0.1$ eV for phonons, ~ 5 eV for plasmons), the electron state is changed considerably. In view of the recent interest in the angular distribution of photoelectrons, it is highly desirable to obtain some quantitative information about the above-mentioned scattering effect. The present study is an effort in this direction.

As a charged particle approaches a surface, a classical description of the electric field is given in terms of image charges. From the point of view of elementary excitations, these electric fields describe the coupling of the electron to surface phonons and surface plasmons. So image-charge theory may be used to derive the matrix element $V_{\vec{k}\vec{k}',\vec{q}}$ which gives the rate an electron scatters from state $\vec{k}\to\vec{k}'$, with the emission of a surface excitation q. Then the scattering rate is derivable from the Fermi Golden rule:

$$\frac{dP}{dt}=\frac{2\pi}{\hbar}\sum_{\vec{k}',\vec{q}}\left|V_{\vec{k}\vec{k}',\vec{q}}\right|^2\delta[E_k-E_{k'}-\hbar\omega(q)] \quad .$$

This scattering rate has the dimension of $(\text{time})^{-1}$. Now if we normalize our wave functions in a box of thickness L, then dP/dt turns out to be proportional to L^{-1}. This is to be expected, as dP/dt is the scattering rate of bulk electrons from surface excitations, and this quantity should vanish for an infinite solid ($L\to\infty$). But as an electron approaches the surface, it is under the influence of the surface scattering during a time L/v_n, where v_n is its velocity normal to the surface, so the scattering probability

$$\lambda=\frac{dP}{dt}\,\frac{L}{v_n}$$

is a dimensionless quantity which is independent of L as $L\to\infty$. λ is the probability that, as the electron goes through the surface, it creates or destroys one surface excitation. It depends upon the electron energy E_k and the angle θ between the velocity vector and the normal to the surface, as well as on the surface parameters such as work function, surface well shape, etc.

We have not studied the processes involving multiple surface excitations. Such a calculation is very difficult if one includes the fact that the electron changes direction and energy after each scattering event. In the approximate theories mentioned above, where the electron trajectory is unchanged by the excitation process, successive excitations all have the same probability. Then one just gets a Poisson distribution

$$P_n=e^{-\lambda}\lambda^n/n! \quad .$$

We emphasize that this distribution does not apply in the low-energy regime, since the electron changes its direction and energy after each excitation.

In summary, the present work differs from the previous studies in that (i) we study the inelastic scattering of electrons owing to surface excitations when the energy of the electrons is not much higher than that of the surface excitation quanta, and (ii) we are interested in the angular dependence of the scattering probability rather than in the loss spectrum.

In Sec. II we discuss the surface modes briefly. The electron-surface mode coupling Hamiltonian is derived in Sec. III. The scattering rate of electrons is calculated in Sec. IV. We have chosen the simplest approximation possible. The solid is assumed to occupy the semi-infinite space $z<0$. The dispersion and damping of the surface modes are neglected. The magnitude and the anisotropy of the calculated scattering rate suggest strongly that this effect must be taken into account explicitly in the analysis of the spectra of outgoing charged particles. In Sec. V some natural questions about our approximations are discussed. We present arguments that the major features of the present results are not sensitive to these approximations. A physical picture, which facilitates our understanding of the results, is also given.

II. SURFACE OPTICAL PHONONS

The theoretical calculations of the subsequent sections give the scattering rate for exciting surface plasmons and surface phonons. The properties of surface plasmons are well known,[6] and need not be reviewed here. Surface optical phonons are not as well known, although their properties are qualitatively similar to those of surface plasmons. So we give a discussion of the eigenfrequencies and polarization fields associated with the surface optical phonons. The retardation effect is included.

The general eigenvalue equation for a surface mode has been derived by Fuchs and Kliewer,[7] and Economou.[8] They show that at a plane interface between two semi-infinite dielectrics with dielectric constants ϵ_i and ϵ_j, the electric fields have the form

$$\vec{E}=-E_0q^{3/2}\left(\frac{\hat{z}}{k_i}-i\frac{\hat{q}}{q}\right)e^{-k_iz+i\vec{q}\cdot\vec{\rho}}, \quad z>0 \qquad (2.1\text{a})$$

$$=E_0q^{3/2}\left(\frac{\hat{z}}{k_j}+i\frac{\hat{q}}{q}\right)e^{k_jz+i\vec{q}\cdot\vec{\rho}}, \quad z<0 \qquad (2.1\text{b})$$

where

$$k_i = (q^2 - \epsilon_i \omega^2/c^2)^{1/2}, \quad k_j = (q^2 - \epsilon_j \omega^2/c^2)^{1/2} \quad ,$$

z is normal to the interface (at $z=0$), and $\vec{p}$ is a two-dimensional position vector in the plane of the surface. ω is a function of $\vec{q}$ to be determined below. The matching of electric and magnetic fields across the interface yields the eigenvalue equation[7,8]

$$k_i/\epsilon_i = -k_j/\epsilon_j \quad . \tag{2.2}$$

At the interface between an ionic crystal and a vacuum, we set $\epsilon_i = 1$ for the vacuum, and for the crystal

$$\epsilon_j = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 - (\omega/\omega_{\mathrm{TO}})^2} \quad , \tag{2.3}$$

where $\epsilon_0, \epsilon_\infty$ are the low- and high-frequency dielectric constants, respectively; and ω_{TO} is the transverse-optical-phonon frequency. The polar dielectric function (2.3) is inserted into (2.2), and the resulting equation is solved to obtain the dispersion relation $\omega(q)$. After squaring (2.2), and collecting terms, one obtains a cubic equation for ω^2,

$$\begin{aligned} \omega^6 \epsilon_\infty(\epsilon_\infty - 1) - \omega^4[\omega_q^2(\epsilon_\infty - 1) + \omega_{\mathrm{TO}}^2(2\epsilon_0\epsilon_\infty - \epsilon_0 - \epsilon_\infty)] \\ + \omega^2[2\omega_q^2(\epsilon_0\epsilon_\infty - 1) + \omega_{\mathrm{TO}}^2\epsilon_0(\epsilon_0 - 1)]\,\omega_{\mathrm{TO}}^2 \\ - \omega_q^2\,\omega_{\mathrm{TO}}^4(\epsilon_0^2 - 1) = 0 \quad , \end{aligned} \tag{2.4}$$

where $\omega_q = cq$. One root of this equation is

$$\omega^2 = \frac{\epsilon_0 - 1}{\epsilon_\infty - 1}\,\omega_{\mathrm{TO}}^2 \quad .$$

This is a bogus nonphysical root. It gives $\epsilon_j = 1$. It is not a solution to (2.2), since solutions to (2.2) must have $\epsilon_j < 0$ if $\epsilon_i = 1$. This bogus root occurs because we squared (2.2), and it is a solution to the squared equation. This root is discarded.

The remaining factors of (2.4) yield a quadratic equation for ω^2. When solved, this gives two branches to the dispersion curve. As discussed by Fuchs and Kliewer, nonradiative surface modes only exist if $\omega_q > \omega(q)$. In our case, the only bound-surface polarization mode has the dispersion relation

$$\omega^2(q) = \tfrac{1}{2}(\tilde{\omega}_q^2 + \omega_{\mathrm{LO}}^2) - \tfrac{1}{2}[(\tilde{\omega}_q^2 + \omega_{\mathrm{LO}}^2)^2 - 4\tilde{\omega}_q^2\omega_{\mathrm{SO}}^2]^{1/2} \ , \tag{2.5}$$

where

$$\tilde{\omega}_q^2 = [(\epsilon_\infty + 1)/\epsilon_\infty](cq)^2 \ , \quad \omega_{\mathrm{LO}}^2 = (\epsilon_0/\epsilon_\infty)\,\omega_{\mathrm{TO}}^2 \ ,$$

$$\omega_{\mathrm{SO}}^2 = \frac{\epsilon_0 + 1}{\epsilon_\infty + 1}\,\omega_{\mathrm{TO}}^2 \quad ,$$

and ω_{SO} is the surface-optical-phonon frequency. Furthermore, a true surface state only exists if $\omega_q > \omega(q)$ which also implies that $\omega(q) > \omega_{\mathrm{TO}}$. This is because $\epsilon < 0$ only for $\omega_{\mathrm{LO}} > \omega > \omega_{\mathrm{TO}}$.

The dispersion relation given by Eq. (2.5) is a new result. It is best illustrated by an example. The dispersion curves for RbI are shown in Fig. 1. The parameters are $\epsilon_0 = 5.5$, $\epsilon_\infty = 2.6$, and $\hbar\omega_{\mathrm{TO}} = 9.2$ meV. The line $\hbar\omega_q$ is also shown. The lower solid line is the surface branch. It ceases to exist at long wavelength $q < \omega_{\mathrm{TO}}/c$, since the mode in this region is radiative. This long-wavelength cutoff was discovered by Fuchs and Kliewer in their numerical solution for dielectric polarization slabs.

At large wave vectors $q \gg \omega_{\mathrm{TO}}/c$, the surface-polariton frequency $\omega(q)$ approaches ω_{SO}. In this limit, where $k_i \to q$, $k_j \to q$, the electric field in (2.1) becomes

$$\lim_{q \gg \omega_{\mathrm{TO}}/c} \vec{\mathrm{E}} = E_0 q^{1/2}\left(i\hat{q} - \frac{z}{|z|}\,\hat{z}\right)e^{-q|z| + i\vec{q}\cdot\vec{\rho}} \quad .$$

Here the electric field is the gradient of $-\phi$,

$$\phi = -E_0 q^{-1/2} e^{-q|z| + i\vec{q}\cdot\vec{\rho}} \quad .$$

The surface phonon creates the potential ϕ. This is the basis fo the electron-phonon interaction derived in Sec. III. This view is not valid for $q < \omega_{\mathrm{TO}}/c$, but this region of phase space is small enough to be ignored.

III. ELECTRON-SURFACE MODE HAMILTONIAN

The electron-surface mode coupling is not an entirely new problem. Roundy and Mills have studied the electron-phonon system starting from crystal potentials.[9] Their main goal is to study the modification of the loss spectrum owing to changes in force constants near the surface. Our

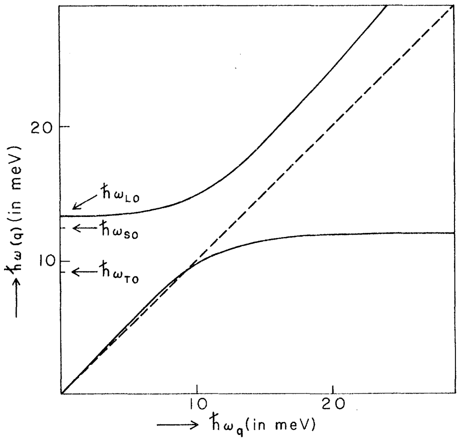

FIG. 1. Dispersion relations for the surface modes of RbI (in the geometry given in Sec. II). The vertical and horizontal axes are $\hbar\omega(q)$ and $\hbar\omega_q$, respectively. The two solid curves are the solutions of Eq. (2.2). The dashed straight line $\hbar\omega(q) = \hbar\omega_q$ is drawn for comparison. Nonradiative surface modes exist only if $\omega_q > \omega(q)$.

objective is quite different, and we prefer to start from a surface-mode view. As this article is being written we are also advised of the work of similar spirits by Lucas, Kartheuser, and Bardo.[10] But again they are interested in loss spectra. Furthermore, they mainly deal with fast electrons. Here we derive an expression that is more appropriate for our purposes.

We consider a semi-infinite medium ($z<0$) in a jellium model. The dispersion of the surface modes is ignored, though its inclusion is not prohibitively difficult. For mode $\vec{q}$, the amplitude of the dielectric polarization at point $R(x, y, z)$ has the form

$$\vec{g}_{\vec{q}}(\vec{R}) = q^{1/2}(\hat{q} - i\hat{z})\, e^{qz + i\vec{q}\cdot\vec{R}}, \quad z<0 \tag{3.1}$$

where $\vec{q}$ is a vector in the xy plane. In the metal case, the local polarization of the electron-ion plasma is also of the form given by Eq. (3.1). In general, if we assume $\vec{g}_{\vec{q}}(\vec{R})$ is a product of an exponentially attenuating part and a plane-wave part, then the condition that there is no polarization charges,

$$\vec{\nabla}\cdot\vec{g}_{\vec{q}}(\vec{R}) = 0 \ ,$$

determines all coefficients to within a normalization constant. The polarization field operator at point $\vec{R}$ is proportional to the sum of amplitudes due to all modes:

$$\vec{P}(\vec{R}) = F\sum_{\vec{q}}\left[\vec{g}_{\vec{q}}(\vec{R})\, a^{\dagger}_{-\vec{q}} + \text{H.c.}\right] \ ,$$

where $a^{\dagger}_{\vec{q}}$ ($a_{\vec{q}}$) is the creation (annihilation) operator for mode $\vec{q}$. The proportional constant F can be determined on physical ground in a way entirely analogous to Kittel's[11] treatment of electron-optical- (bulk) phonon interaction. For normalization purposes we use a box of cross section A and length $2L$, with $0<z<L$ being the free space and $-L<z<0$ the solid. Then we obtain

$$F = \left[\left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)\frac{\hbar\omega_s}{2\pi A}\right]^{1/2} \quad \text{for dielectrics}$$

and (3.2)

$$F = (\hbar\omega_s/4\pi A)^{1/2} \quad \text{for metals} \ ,$$

where $\hbar\omega_s$ is the energy of the surface-mode quanta. The details of the calculation are given in Appendix A.

An electron is coupled with the surface modes through the term

$$H_{\text{int}} = \int d^3r\, \psi^{\dagger}(\vec{r}) \int d^3R\, V(\vec{r}-\vec{R})\, \psi(\vec{r}) \ , \tag{3.3}$$

where

$$V(\vec{r}-\vec{R}) = e(\vec{r}-\vec{R})\cdot\vec{P}(\vec{R})/|\vec{r}-\vec{R}|^3 \ .$$

We set out to reduce H_{int} to the more convenient form

$$H_{\text{int}} = \sum_{\vec{k}\vec{k}'\vec{q}} V_{\vec{k}\vec{k}'\vec{q}}\, c^{\dagger}_{\vec{k}'} c_{\vec{k}}\, \phi_{\vec{q}} \ ,$$

where $c^{\dagger}_{\vec{k}}$ and $c_{\vec{k}}$ are creation and destruction operators for the electronic state $\vec{k}$, respectively, $\phi_{\vec{q}} = a_{\vec{q}} + a^{\dagger}_{-\vec{q}}$ is the phonon field operator, and $V_{\vec{k}\vec{k}'\vec{q}}$ is a scalar matrix element. We assume the motion in xy plane is free, and expand $\psi(\vec{r})$ in terms of eigenfunctions:

$$\psi(\vec{r}) = \sum_{\vec{k}} c_{\vec{k}}\, e^{i\vec{k}_{\parallel}\cdot\vec{r}} A^{-1/2} u_{k_3}(z) \ , \tag{3.4}$$

where $\vec{k}_{\parallel} = \vec{k} - (\vec{k}\cdot\hat{z})\hat{z}$ is the component of $\vec{k}$ in the xy plane, $k_3 = \vec{k}\cdot\hat{z}$ is the z component of $\vec{k}$, and $u_{k_3}(z)$ is the normalized wave function for z motion. On combining Eqs. (3.1)–(3.4), we obtain

$$H_{\text{int}} = \sum_{\vec{k}\vec{k}'\vec{q}} A^{-1} eF \int d^3r\, d^3R\, c^{\dagger}_{\vec{k}'} c_{\vec{k}}\, e^{i(\vec{k}_{\parallel} - \vec{k}'_{\parallel})\cdot\vec{r}}$$
$$\times\, u_{k_3}(z)\, u^{*}_{k'_3}(z)\, \frac{\vec{r}-\vec{R}}{|\vec{r}-\vec{R}|^3}\cdot\vec{g}_{\vec{q}}\, a^{\dagger}_{-\vec{q}} + \text{H.c.}$$

It is straightforward to perform the xy and $\vec{R}$ integrals, giving

$$H_{\text{int}} = \sum_{\vec{k}\vec{k}'\vec{q}} V_{\vec{k}\vec{k}'\vec{q}}\, c^{\dagger}_{\vec{k}'} c_{\vec{k}}\, \phi_{\vec{q}} \ , \tag{3.5}$$

where

$$V_{\vec{k}\vec{k}'\vec{q}} = 2\pi eFq^{-1/2}\left[\int_{-L}^{L} dz\, e^{-q|z|}\, u_{k_3}(z)\, u^{*}_{k'_3}(z)\right]\delta_{\vec{k}'_{\parallel},\, \vec{k}_{\parallel}+\vec{q}} \ .$$

This is the interaction that we will use in the subsequent calculations. Some questions concerning the approximations in this section will be discussed in Sec. V.

IV. SCATTERING OF ELECTRONS OWING TO ELECTRON-SURFACE MODES COUPLING

An electron approaching or leaving the solid surface suffers scattering due to the interaction given by Eq. (3.5). At this point we have to specialize to a specific energy band. We will assume that the electron in question is in a free-electron-like band with effective mass m^*. For the crystal potential we choose the simplest form, a step function

$$V = V_0, \quad z>0$$
$$= 0, \quad z<0 \ .$$

V_0 is measured with respect to the bottom of the band. In a simple metal V_0 is roughly the sum of Fermi level and the work function. The wave functions $u_{k_3}(z)$ are easily found to be *for unbound states* ($E_{k_3} = \hbar^2 k_3^2/2m^* > V_0$), *outgoing states*:

$$u_{k_3}(z) = (2L)^{-1/2}(e^{ik_3 z} + Re^{-ik_3 z}), \quad z<0$$
$$= (2L)^{-1/2}\, T e^{ip_3 z/\hbar}, \quad z>0$$

where

$$p_3 = \hbar(k_3^2 - 2m^* V_0/\hbar^2)^{1/2}, \qquad R = \frac{\hbar k_3 - p_3}{\hbar k_3 + p_3} \ ,$$

$$T=1+R;$$

for unbound incoming states:

$$u_{k_3}(z)=(2L)^{-1/2}(\hbar k_3/p_3)^{1/2}T'e^{-ik_3z}, \qquad z<0$$

$$=(2L)^{-1/2}(\hbar k_3/p_3)^{1/2}(e^{-ip_3z/\hbar}+R'e^{ip_3z/\hbar}), \qquad z>0$$

where $R'=-R$ and $T'=1+R'$; *and for bound states* $(E_{k_3}=\hbar^2k_3^2/2m^*<V_0)$:

$$u_{k_3}(z)=(2/L)^{1/2}\sin(k_3z+\delta), \quad z<0$$

$$=(2/L)^{1/2}T''e^{-\alpha z}, \qquad z>0$$

where

$$\alpha=(2m^*V_0/\hbar^2-k_3^2)^{1/2}, \quad \delta=\tan^{-1}(-k_3/\alpha),$$

$$T''=\sin\delta .$$

These wave functions are used to evaluate $V_{\vec{k}\vec{k}',\vec{q}}$ in Eq. (3.5). The scattering rate for an electron in state $\vec{k}$ is, in the first Born approximation,

$$\frac{dP}{dt}=\frac{2\pi}{\hbar}\sum_{\vec{k}',\vec{q}}|V_{\vec{k}\vec{k}',\vec{q}}|^2\,\delta(E_k-E_{k'}-\hbar\omega_s). \qquad (4.1)$$

By writing out $V_{\vec{k}\vec{k}',\vec{q}}$ explicitly it is easily seen that $dP/dt\sim 1/L$, which is a necessary result when one recalls that for large L the surface modes should not lead to significant "bulk" damping. For convenience we define a dimensionless quantity

$$\lambda=\frac{dP}{dt}\frac{L}{v_n},$$

where $v_n=\hbar k_3/m^*$. λ is a measure of the probability that an electron will suffer an inelastic scattering after traveling a distance L. We have confined ourselves to the low-temperature region so only phonon or plasmon emission processes contribute.

If θ is the angle between the electron vector $\vec{k}$ and the normal to the surface, then for every electron energy $E_k>V_0$, there is an angle

$$\theta_k=\cos^{-1}(V_0/E_k).$$

When $\theta>\theta_k$, the electron is in a bound state. For $\theta<\theta_k$, the electron can be in either of the two unbound states. We have calculated λ for the outgoing states and the bound states. In most cases the q sum can be expressed in terms of the elliptic integral of the third kind or the derivatives thereof. Details are given in Appendix B. The $\theta=0$ case is particularly easy to evaluate. It serves as a quick estimate and also provides a check for our calculation. For the various parameters we have chosen (m_e is the electron mass) in the dielectric case

$$m^*=0.2m_e, \quad \hbar\omega_s=0.1\text{ eV}, \quad V_0=1.6\text{ eV},$$

$$\epsilon_0=10, \qquad \epsilon_\infty=5, \qquad E_k=1.75\text{ and }3.75\text{ eV};$$

in the metal case

$$m^*=1m_e, \quad \hbar\omega_s=4\text{ eV}, \quad V_0=5.6\text{ eV},$$

$$E_k=9.75\text{ and }11.75\text{ eV}.$$

One may wonder why in the metal case we do not specify the Fermi level E_F. The reason is that the result does not depend on E_F at all as long as

$$E_k-\hbar\omega_s>E_f,$$

because all k_3' states are available. This is the case for photoemission experiments in simple metals if the incident photon is of energy $\gtrsim 6-7$ eV. We have confined ourselves to this case.

The result of our calculation is shown in Fig. 2. We have found that Lucas and Sunjic's[4] result is an estimate of the right order, when the final states k_3' are limited to the unbound states. However, the contribution from the bound states in many cases far outweighs that from the unbound states. Another interesting observation is that λ shows a peak near θ_k. In other words, electrons that can barely climb out the potential barrier or barely fail to do so are scattered most strongly. That λ becomes large as $\theta\to\frac{1}{2}\pi$ is not really significant. We have chosen to plot the scattering probability in a time elapse $t=L/v_n$, which is a measure of the time the electron traverses the sample in the normal direction. This time scale becomes large when $\theta\to\frac{1}{2}\pi$ since $v_n\to 0$. This apparent anomaly would not appear if we choose a different time scale, L/v_k $[v_k=(2E_k/m^*)^{1/2}]$, for example, while there would be little change in other characteristics.

There is yet little data on the angular dependence of photoelectrons. Of the experimental work that

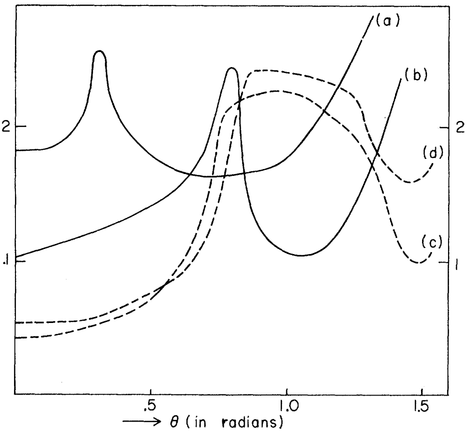

FIG. 2. Plots of λ vs θ. The solid curves refer to insulators and the left-hand vertical scale. The dashed curves correspond to metals and the right-hand scale. The electron energy in eV is for curve (a) 1.75, (b) 2.75, (c) 9.75, and (d) 11.75. Other parameters are given in Sec. IV.

has been reported,[2] our calculation may be too crude to compare with the actual data. However, the magnitude and θ dependence of λ bear out our contention that this heretofore often neglected effect deserves a much more detailed study in the spectroscopy of charged particles emerging from a solid.

V. DISCUSSION

In view of the approximations made in the calculations, it is natural to ask what features of our results will remain intact in a more sophisticated study. In this section we reason that major aspects of our results are insensitive to the approximations. In particular, the peak of λ near θ_k can be described by a physical picture without ever referring to detailed band parameters.

The important questions that we should address ourselves to are the following:

(*i*) *Effect of scattering from bulk excitations.* We have not studied the scattering from bulk excitations. One may wonder whether that effect would overshadow the present result. We feel that it is unlikely. The reason is that there have not been great difficulties in distinguishing surface and bulk effects in loss spectra.[2-5] Neither effect seems to be completely dominating in magnitude. We expect this would also be the case with the angular distribution. A definite answer, however, should come from a direct calculation.

(*ii*) *Use of free-electron wave functions.* It is well known that in general the lattice potentials are essential to determine the low-energy electron states. Some recent work on low-energy electron diffraction and surface-plasmon dispersion in Al has indeed taken this fact into account to obtain better agreement with experiments.[12] We mentioned earlier, however, that the present study is concerned with simple metals (as also evidenced by our choice of parameters), where the free-electron wave functions are quite acceptable. For other metals we should still expect a peak in λ. This point will become clearer later on, after we see the physical nature of the peak.

(*iii*) *Adequacy of our treatment of the electron-plasmon coupling.* The electron-plasmon coupling is a complicated subject and has been studied extensively. One recent review is by Feibelman, Duke, and Bagchi.[13] We believe, however, the result of our simple calculation is essentially correct.

The strength of the coupling has not been unduly exaggerated, as there is the definite physical guideline that this coupling leads to the image potential. The detailed functional form for F will certainly be modified when damping and dispersion of the modes are included. In general damping tends to smooth out any abrupt contours. But in Fig. 2 there is no exceptionally sharp features. Besides, owing to the energy and momentum conservation, the q sum in Eq. (4.1) comes from a limited region in q space. The usually mild dispersion should not change the result significantly.

The electron operators $(c_{\vec{k}}^{\dagger},\ c_{\vec{k}})$ actually do not commute with $\phi_{\vec{q}}$, the plasmon field operator. The latter must be a linear combination of terms of the form $c_{\vec{k}'}^{\dagger} c_{\vec{k}}$, where $\vec{k}_{\parallel}' = \vec{k}_{\parallel} + \vec{q}$, owing to the translational invariance. Because of the large number of terms, the relative error arising from the neglect of this noncommutivity is only of the order $1/N$, N being the number of k states in the band.

(*iv*) *Physical nature of the peak of* λ. The electron field associated with surface modes attenuates exponentially when one moves away from the surface in either direction. For an electron with $\theta = \theta_k - \delta$, the trajectory is similar to that of a light ray with incident angle just below θ_c, the critical angle. The trajectory outside the solid is almost parallel to the surface. The electron spends so much time near the surface, where the field is the highest, that it is scattered strongly. On the other hand, an electron with $\theta = \theta_k + \delta$ corresponds to a totally reflected ray. The trajectory does not lie near the surface, and there is less scattering. These simple considerations explain qualitatively the peak of λ at $\theta \sim \theta_k$ in insulators. For metals there is further complication in that E_k and $\hbar\omega_s$ are of the same order. An electron can emit $\hbar\omega_s$ and the final state has a k_3' much smaller than that of the initial state. Thus even if θ is not in the immediate neighborhood of θ_k, the trajectory corresponding to the final state can have significant portions near the surface. Since the matrix elements depend as much on the initial states as on the final states, this explains why λ has a rather broad peak for metals.

The above picture helps us to understand the nature of the behavior of λ. It is always to be remembered, however, that the concept of trajectory is not a precise one for low-energy electrons and should be used with caution.

We can now say something about the case of metals where the nearly-free-electron model does not apply. λ as a function of angle will still have a peak when the electron is moving in such a direction that it can barely climb out the potential barrier. The peak will be broad as long as E_k and $\hbar\omega_s$ are of the same order.

In passing we may add that based on our physical picture, one would expect that in the reflection case the electrons incident in the grazing direction will be scattered most effectively. This has indeed been found by Lucas and Sunjic.[5] In fact, the scattering is so strong that multiplasmon processes contribute significantly. Their calculation is for fast electrons, for which the concept of classical trajectory is on a much more solid ground.

We conclude that the major features of our results, the large magnitude and the angular dependence of λ, are well founded and are unlikely to be modified appreciably by more sophisticated calculations.

APPENDIX A : DETERMINATION OF F

We shall calculate the extra interaction between the solid and a charge Q outside owing to one-phonon or -plasmon exchange. It has been shown that surface modes are solely responsible for the image charges.[14] We put an external charge Q at position $(0, 0, z_1)$, $z_1 > 0$. We obtain F in terms of known physical quantities by comparing our expression for the extra interaction energy to that owing to image charges,

$$\Delta E = -Q^2\left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\ \frac{1}{2z_1}\right) \text{ for dielectrics}$$

$$= -Q^2/4z_1 \text{ for metals,} \tag{A1}$$

where ϵ_0, ϵ_∞ are the dielectric constants at low and high frequencies, respectively.

The polarization field associated with the mode $\vec{q}$ is

$$\vec{P} = F\vec{g}_{\vec{q}} = F q^{1/2}(\hat{q} - i\hat{z})\, e^{i\vec{q}\cdot\vec{R}+qz}, \quad z < 0 .$$

There is no volume charge. At the dielectric surface the charge density is

$$\sigma = (\vec{P}\cdot\hat{z}) = -ie^{i\vec{q}\cdot\vec{R}} F q^{1/2} = -ie^{i\vec{q}\cdot\vec{\rho}} F q^{1/2} .$$

The Z component of electric field at $(0, 0, z_1)$ is

$$E_z = \int d^2\rho\, \frac{z_1}{(\rho^2 + z_1^2)^{3/2}}\, (-iFq^{1/2} e^{i\vec{q}\cdot\vec{\rho}})$$

$$= -2\pi i F q^{1/2} e^{-qz_1} .$$

The potential energy φ is then

$$\varphi(0, 0, z_1) = -2\pi i F q^{-1/2} e^{-qz_1} .$$

The extra interaction energy between the charge Q and the solid is

$$\Delta E = \sum_{\vec{q}} \frac{\langle 0 | Q\varphi(0,0,z_1) | 1\rangle\langle 1 | Q\varphi(0,0,z_1) | 0\rangle}{-\hbar\omega_s}$$

$$= -\frac{Q^2}{\hbar\omega_s}\int A q\, dq\, d\phi\, (2\pi)^{-2} (2\pi F q^{-1/2} e^{-qz_1})^2$$

$$= -\frac{Q^2}{\hbar\omega_s}\left(\frac{A\pi}{z_1}\right) F^2 .$$

This should be identical to (A1). Therefore we obtain

$$F = \left[\left(\frac{1}{\epsilon_\infty + 1} - \frac{1}{\epsilon_0 + 1}\right)\frac{\hbar\omega_s}{2\pi A}\right]^{1/2} \text{ for dielectrics}$$

$$= (\hbar\omega_s/4\pi A)^{1/2} \text{ for metals.}$$

APPENDIX B : REDUCTION OF THE MULTIPLE SUM

We want to evaluate

$$S = \sum_{\vec{k}'\vec{q}} | V_{\vec{k}\vec{k}'\vec{q}} |^2\, \delta(E_k - E_{K'} - \hbar\omega_s) . \tag{B1}$$

We choose $\vec{k}_\parallel$ to be in the x direction. $\vec{q} = (q, \phi)$ in polar coordinates. The factor $\delta_{\vec{k}'_\parallel, \vec{k}_\parallel+\vec{q}}$ eliminates $\vec{k}'_\parallel$ sum and we have

$$S = \sum_{k'_3\vec{q}} | V_{\vec{k}\vec{k}'\vec{q}} |^2\, \delta\left(\frac{\hbar^2(k_\parallel^2 + k_3^2)}{2m^*} - \frac{\hbar^2(k_\parallel^2 + 2k_\parallel q\cos\phi + q^2 + k_3'^2)}{2m^*} - \hbar\omega_s\right)$$

$$= \frac{2LA}{(2\pi)^3}\int dk'_3\, q\, dq\, | V_{\vec{k}\vec{k}'\vec{q}} |^2_{\vec{k}'_\parallel = \vec{k}'_{\parallel 0}} \left| \frac{\hbar^2 q k_\parallel \sin\phi_0}{m^*} \right|^{-1} ,$$

where

$$\cos\phi_0 = \left(\frac{\hbar^2 q k_\parallel}{m^*}\right)^{-1}\left(\frac{\hbar^2 k_3^2}{2m^*} - \frac{\hbar^2 q^2 + \hbar^2 k_3'^2}{2m^*} - \hbar\omega_s\right)$$

and

$$\vec{k}'_{\parallel 0} = \vec{k}_\parallel + \vec{q}_0 ,$$

with $\vec{q}_0 = (q, \phi_0)$ in polar coordinates. The restriction $-1 \leqslant \cos\phi_0 \leqslant 1$ determines the limits of q integration. For convenience we define a quantity

$$\gamma = \left(\frac{2m^*}{\hbar^2}\quad E_k - \frac{\hbar^2 k_3'^2}{2m^*} - \hbar\omega_s\right)^{1/2} .$$

Then the lower and upper limits are

$$q_1 = |\gamma - k_\parallel| \quad\text{and}\quad q_2 = \gamma + k_\parallel ,$$

respectively. With a little algebraic manipulation the sum S can be rewritten as

$$S = \frac{2LA}{(2\pi)^3}\int dk'_3\, dq\, | V_{\vec{k}\vec{k}'\vec{q}} |^2 q[(q^2 - q_1^2)(q_2^2 - q^2)]^{-1/2} .$$

By separating $| V_{\vec{k}\vec{k}'\vec{q}} |^2$ into partial fractions, it is found that

$$S = \int dk'_3\, dq \sum_i a_i K_i(q) ,$$

where a_i is independent of q, and K_i is of one of the following forms:

$$K_1 = \frac{1}{q + b_1}\kappa , \quad K_2 = \frac{1}{q^2 + b_2^2}\kappa ,$$

$$K_3 = \frac{q}{q^2 + b_3^2}\kappa , \quad K_4 = \frac{1}{(q^2 + b_4^2)^2}\kappa , \quad K_5 = \frac{q}{(q^2 + b_3^2)^2}\kappa ,$$

where $\kappa = [(q^2 - q_1^2)(q_2^2 - q^2)]^{1/2}$ and b_i is independent of q. Depending on whether k'_3 corresponds to an outgoing, incoming, or bound state, a_i and b_i assume different functional forms. We omit their explicit expressions here. Next we define

$$I_i = \int_{q_1}^{q_2} K_i(q)\,dq \;.$$

We will now discuss I_3 and I_5, as they are elementary integrals. I_1 can be reduced in the following way:

$$I_1 = \int_{q_1}^{q_2} dq\, \frac{q-b_1}{q^2-b_1^2}\, K = I_{11} - b_1 I_{12} \;,$$

where

$$I_{11} = \int_{q_1}^{q_2} dq\, \frac{q}{q^2-b_1^2}\, \kappa$$

and

$$I_{12} = \int_{q_1}^{q_2} dq\, \frac{1}{q^2-b_1^2}\, \kappa \;.$$

The principal part of the integral is to be taken if b_1 lies between q_1 and q_2. I_{11} is again elementary. I_{12} is of the same form as I_2. They can be expressed in terms of known functions by using the identity[15]

$$\int_b^a dt\, \frac{1}{t^2-p}\, [(a^2-t^2)\,(t^2-b^2)]^{-1/2} = \frac{1}{a}\, \frac{1}{a^2-p}\, \Pi\left[\frac{\pi}{2}, \left(\frac{a^2-b^2}{a^2}\right)^{1/2}\right] ,$$

where Π is the elliptic integral of the third kind. Finally, we have

$$I_4 = \int_{q_1}^{q_2} dq\, \frac{1}{(q^2+b_4^2)^2}\, \kappa = \frac{1}{q_2}\, \frac{1}{(q_2^2+b_4^2)^2}\, V_2 \,,$$

where

$$V_2 = \int_0^{u_1} \frac{du}{(1-\alpha^2\,\mathrm{sn}u)^2}$$

with

$$\alpha^2 = \frac{q_2^2-q_1^2}{q_2^2+q_1^2}\,, \quad k^2 = \frac{q_2^2-q_1^2}{q_2^2}\,, \qquad \mathrm{sn}\,u_1 = 1$$

has also been evaluated.[16] Thus we have reduced all I_i to known functions. The k_3' integral has to be performed numerically. When the electron vector $\vec{k}$ is normal to the surface, the q integral can be done trivially, thanks to the δ functions. This serves as a check to our calculations.

---

*Work supported by the National Science Foundation.

[1] Partial list: G. D. Mahan, Phys. Rev. B 2, 4334 (1970); W. L. Schaich and N. W. Ashcroft, *ibid.* 3, 2452 (1971); R. Y. Koyama and N. V. Smith, *ibid.* 2, 3049 (1970); D. C. Langreth, *ibid.* 3, 3120 (1971).

[2] N. V. Smith and W. E. Spicer, Phys. Rev. Letters 23, 769 (1969); F. Wooten, T. Huen, and H. V. Minsor, Phys. Letters 36A, 351 (1971); T. Gustafsson, P. O. Nilsson, and L. Wallden, *ibid.* 37A, 121 (1971).

[3] A. A. Lucas and M. Sunjic, Phys. Rev. Letters 26, 229 (1971); K. L. Ngai and E. N. Economou, Phys. Rev. B 4, 2132 (1971); A. A. Lucas and E. Kartheuser, *ibid.* 1, 3588 (1970).

[4] A. A. Lucas and M. Sunjic, Invited Paper at the International Conference on Solid Surfaces, Boston, 1971 (unpublished).

[5] M. Sunjic and A. A. Lucas, Phys. Rev. B 3, 719 (1971).

[6] R. M. Ritchie, Phys. Rev. 106, 874 (1957).

[7] R. Fuchs and K. L. Kliewer, Phys. Rev. 140, A2076 (1965); K. L. Kliewer and R. Fuchs, *ibid.* 144, 495 (1966); R. Fuchs and K. L. Kliewer, *ibid.* 150, 573 (1966).

[8] E. N. Economou, Phys. Rev. 182, 539 (1969).

[9] V. Roundy and D. L. Mills, Phys. Rev. B 5, 1347 (1972).

[10] A. A. Lucas, E. Kartheuser, and R. G. Bardo, Solid State Commun. 8, 1075 (1970).

[11] C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1967), pp. 137–139.

[12] G. E. Laramore, C. B. Duke, A. Bagchi, and A. B. Kunz, Phys. Rev. B 4, 2058 (1971); G. E. Laramore and C. B. Duke, *ibid.* 5, 267 (1972); A. Bagchi, C. B. Duke, P. J. Feibelman, and J. O. Porteus, Phys. Rev. Letters 27, 998 (1971).

[13] P. J. Feibelman, C. B. Duke, and A. Bagchi, Phys. Rev. B 5, 2436 (1972).

[14] A. A. Lucas and M. Sunjic (unpublished); G. D. Mahan, Phys. Rev. B 5, 739 (1972).

[15] Special case of (218.02) in P. F. Byrd and M. D. Friedman, in *Handbook of Elliptic Integrals for Engineers and Physicists* (Springer-Verlag, Berlin, 1954).

[16] Reference 15, (218.13) and (336.02).