Many-Body Formalism for Photoemission Studies*

J. I. Gersten and N. Tzoar
Department of Physics, City College of the City University of New York, New York, New York 10031
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A many-body formalism suitable for application to photoemission or other surface-related problems is developed. It allows one to include, in a simplified way, effects of bulk plasmons, surface plasmons, and electron-hole pairs. A set of optical potentials is obtained which describe the virtual excitation of such modes of the solid. The optical potentials are energy dependent and vary as a function of the distance from the surface. Deep in the crystal they tend to an asymptotic value independent of the location. Characteristic oscillations appear as one approaches the surface region. A cusp at the surface occurs which is followed by a rapid decay of the potential into the vacuum region.

I. INTRODUCTION

While the bulk properties of solids have been the object of experimental and theoretical investigation for decades, it has not been until fairly recently that surface properties have undergone such a similar attack. Not until the techniques for surface preparation had been perfected, were reproducible and accurate experimental data able to be extracted from laboratory measurements. The fact that several independent experimental techniques now give consistent information relating to such a physical property as the electronic density of states, lends credence to the belief that the hurdle of obtaining meaningful data has finally been surmounted. The methods available to physicists for studying surfaces now include such techniques as photoemission, photoabsorption, low-energy-electron diffraction, inelastic-electron-loss spectroscopy, tunneling, field emission, ion-neutralization spectroscopy, and electroreflectance. All these techniques share the common characteristic that the projectile (be it photon or electron) is capable of coupling to the electronic excitations of the solid.

In giving a first interpretation to experimental results one is usually tempted to employ a one-electron picture. One imagines a single electron interacting with a background array of ion cores. This lattice is taken to terminate in some fashion at the surface of the crystal. Thus, for example, in photoemission one has the following crude description of the phenomenon. The incident photon is absorbed by an electron and the electron is promoted to some higher-energy level. If the electron were not under the influence of external forces this process would be forbidden, since one could not simultaneously conserve energy and momentum. However, the lattice provides a momentum reservoir in which integral multiples of reciprocal-lattice vectors can be supplied to the electronic momentum to allow it to be conserved. In addition, the termination of the lattice provides a continuous spectrum of wave vectors which could likewise maintain the momentum-conservation constraint. A comparison of the predictions of such a model with experiment is likely to meet with only partial success. While it may be possible to identify features in the photoemission spectrum with certain predicted features, such as peaks in the electronic density of states, the model fails in several respects. First, it does not give an accurate accounting for the absolute photo yield. Thus serious discrepancies are likely to occur in comparing the number of electrons emitted per incident photon calculated by such a model and measured in the laboratory. Second, new features often appear in the electronic spectrum which are completely unexplainable in the one-electron picture.

The difficulties cited above are not limited to photoemission alone but occur to a greater or lesser extent in the other experimental techniques which were enumerated. The origin of these problems, of course, lies in the fact that although the electron-electron potential is relatively weak, it is of long range, so electrons strongly scatter from each other. Thus inadequacies of the one-electron picture point to the necessity for solving the many-body problem. Unfortunately this presents its own challenges. One now has to worry about having the electron colliding with the other electrons and producing electron-hole pairs, bulk plasmons, and surface plasmons. Thus the number of elementary processes begins to proliferate as does the number of integrations that one must perform in the course of a given calculation. The problem rapidly becomes unwieldy and it grows clear that the solution to the many-body problem cannot be pushed through without great effort. A further pessimistic note is sounded by the fact that the existence of a surface permits neither the simplification of using a plane-wave basis, as one would employ in free space, nor a Bloch-wave basis, as one would use in describing bulk properties. Thus one expects that the integrations involved in calculating the matrix elements associated with such elementary processes would likewise be cumber-

some. It becomes clear that if substantial progress is to be made in incorporating many-body effects into surface-physics-related problems, some simplifying assumption will have to be made.

An advance in simplifying the many-body treatment for an electron gas has been made by Overhauser.[1] He showed that it was possible to describe the density fluctuations by a single quasimode excitation which would simultaneously account for bulk plasmon and electron-hole pair production in bulk crystals. In fact the properties of this quasimode were shown to be determined by a knowledge of the static bulk dielectric properties of the medium. These properties, of course, are given by detailed many-body calculations. One of the objectives of the present paper will be to extend this quasimode concept to the semi-infinite crystal. Thus we will introduce two elementary-excitations—bulk-quasimode-excitations (BQM) and surface quasimode excitations (SQM). The former excitations will be quite similar to the entities introduced by Overhauser while the latter modes will account for the surface plasmons. One might ask if such drastic approximations are at all justified. While the ultimate justification lies in a comparison of theory with experiment, one might make the following remark. The experimentally observable quantity, such as the photoelectron spectrum in photoemission studies, is generally obtained after many integrations over intermediate sets of states associated with the Feynman diagrams corresponding to specific processes. If one replaces these intermediate states by a crude approximation to them, such as a single quasimode, it is quite possible that the photoelectron spectrum would not be radically perturbed. This will especially be true if certain key sum rules are obeyed by the quasimodes. As Overhauser[1] has shown, the elementary excitations that he defines maintain the oscillator-strength sum rule. Thus by a small sacrifice in accuracy one is able to buy a large gain in computational simplicity, and hopefully make the problem tractable.

A second important advance in simplifying the surface problem has been made by Ritchie and Marusak.[2] They showed that it was possible to obtain a reasonable description of surface plasmons in terms of the dielectric properties of the medium by making a few simple assumptions, such as assuming specular reflection. In this paper the method of approach of Ritchie and Marusak will be extended to include the coupling of electrons to the surface plasmons. This will then mesh, in a very natural way, with the surface-quasimode concept. Here again we note that some debate exists in the literature[3] as to the validity of the dispersion relation for surface plasmons obtained by the above authors. However, one can again invoke the line of reasoning that says that the quantities of experimental interest in surface physics are not so much the detailed dispersion relations, but quantities which are rather complicated functionals of them. Thus while the fine details of the dispersion relations may vary from theory to theory, these variations are, in all likelihood, washed out by the time one has computed an observable quantity.

Returning to our example of photoemission, it now appears that we will be able to augment the one-electron processes by ones in which the electrons can couple to loss modes of the solid and emit BQM or SQM excitations. The question one would ask is: Does this change, in any way, the original one-electron process? The answer is that it does. One can give a formal explanation of this alteration in terms of a renormalization of the one-electron propagator by virtual emission and absorption of the SQM or BQM excitations. A major goal of the present paper will be to show how this renormalization can be carried out by introducing appropriate optical potentials.

The present paper represents a generalization of the work of one of the authors[4] in several respects. Previously the coupling to surface plasmons and bulk plasmons in the long-wavelength limit was obtained. In order to apply those calculations to surface studies one has two problems. First of all, one must cut off the plasmon coupling in some manner when the plasmon dispersion curve intersects the electron-hole-production domain. This occurs at high wave numbers. This problem has been considered in some detail in the literature.[5] Second, one must still incorporate electron-hole excitations as a possible loss mechanism into the theory. By introducing the quasimodes of the present paper both these problems are solved simultaneously.

In Secs. II–VI we proceed as follows. First we discuss the quantization of quasimode excitations in a semi-infinite medium. Then we consider the coupling of electrons to bulk quasimodes. Following this is a discussion of the coupling of electrons to surface quasimodes. Then the problem of constructing the optical potential is attacked. Finally a discussion of the results of calculation is presented.

This work represents the first in a series of papers relating to photoemission studies. We have decided to divorce it from specific photoemission calculations because we believe that the results derived in this paper transcend applicability to just photoemission. Thus we believe that the concepts and results dealt with in this paper should be useful in discussing all surface-related problems. The treatment of specific photoemission problems has been deferred to subsequent papers in this series.

II. EXCITATIONS IN SEMI-INFINITE DIELECTRIC

As long as one is willing to neglect the so-called retardation terms, the excitations of a semi-infinite crystal can be characterized by a scalar potential. This approximation is valid except at very long wavelengths. Following Nozières and Pines[6] the crystals will be characterized as a semi-infinite dielectric. All the electronic properties of the crystal are to be describable in terms of the dielectric function $\epsilon(\vec{k}, \omega)$. Thus we shall think of our elementary excitations as potential waves propagating through a dielectric medium. As the wave propagates, a cloud of induced polarization charge undulates at the characteristic frequency ω and wave number $\vec{k}$.

Let us make a Fourier expansion of the electrostatic potential $\Phi(\vec{r}, t)$:

$$\Phi(\vec{r}, t) = \int d\vec{k}\, d\omega\, e^{i(\vec{k}\cdot\vec{r}-\omega t)}\, \Phi(\vec{k}, \omega). \tag{2.1}$$

The vacuum region will be taken to be the domain $z > 0$ while the crystal occupies the space $z < 0$. Since Laplace's equation must be satisfied in the vacuum, it follows that

$$0 = \int d\vec{k}\, d\omega\, e^{i(\vec{k}\cdot\vec{r}-\omega t)}\, k^2\, \Phi(\vec{k}, \omega), \tag{2.2}$$

for all $z > 0$. Hence $U(k_z) \equiv k^2\, \Phi(\vec{k}, \omega)$ is an analytic function of k_z in the upper half k_z plane. Inserting this into Eq. (2.1) and closing the contour in the upper half k_z plane leads to

$$\Phi(\vec{r}, t) = \int d^2k_\perp\, d\omega\, e^{i(\vec{k}_\perp\cdot\vec{r}-\omega t)}\, A(k_\perp, \omega)\, e^{-k_\perp z}, \tag{2.3}$$

where we have let $A(\vec{k}_\perp, \omega) \equiv (\pi/k_\perp)\, U(ik_\perp)$. One notes that in the limit as $z \to \infty$ the electrostatic potential remains well behaved. In the crystal domain ($z < 0$) let us expand Φ as the sum of two terms. The first will be chosen to vanish at the surface. Hence it can be expanded in terms of a Fourier sine integral:

$$\Phi_1(\vec{r}, t) = \int d^2k_\perp \int_0^\infty dk_z \int d\omega \times B(\vec{k}, \omega) \sin k_z z\, e^{i(\vec{k}_\perp\cdot\vec{r}-\omega t)}. \tag{2.4}$$

The range of integration on k_z has been restricted to the domain $k_z \geq 0$ in order to avoid a double counting of equivalent states. Since our electrostatic potential has been expressed in the form

$$\Phi(\vec{r}, t) = \Phi_1(\vec{r}, t) + \Phi_2(\vec{r}, t), \tag{2.5}$$

the choice of $\Phi_2(\vec{r}, t)$ is somewhat arbitrary. However, we know that $\Phi(\vec{r}, t)$ must be continuous across the surface. For the sake of convenience we choose $\Phi_2(\vec{r}, t)$ to be a reflection of $\Phi(\vec{r}, t)$ in the vacuum, which would agree with the known behavior of surface plasmons. Thus,

$$\Phi_2(\vec{r}, t) = \int d^2k_\perp\, d\omega\, e^{i(\vec{k}_\perp\cdot\vec{r}-\omega t)} A(\vec{k}_\perp, \omega)\, e^{+k_\perp z}. \tag{2.6}$$

Thus the expansion for $\Phi(\vec{r}, t)$ valid over all space is

$$\Phi(\vec{r}, t) = \int d^2k_\perp \int d\omega \int_0^\infty dk_z\, B(\vec{k}, \omega) \times \sin k_z z\, \Theta(-z)\, e^{i(\vec{k}_\perp\cdot\vec{r}-\omega t)} + \int d^2k_\perp \int d\omega\, A(\vec{k}_\perp, \omega) \times e^{-k_\perp |z|}\, e^{i(\vec{k}_\perp\cdot\vec{r}-\omega t)}. \tag{2.7}$$

Here $\Theta(z)$ is defined as zero for negative z and as unity for positive z. From the reality of Φ it follows that $B(-\vec{k}_\perp, k_z, -\omega) = B^*(\vec{k}_\perp, k_z, \omega)$ and $A(-\vec{k}_\perp, -\omega) = A^*(\vec{k}_\perp, \omega)$.

So far no approximation has been made. Let us now utilize some of our knowledge of the physics of the problem to simplify the above description. If one examines the long-wavelength excitations one finds that the dominant mode is the plasmon mode. As pointed out by Overhauser, [1] most of the oscillator-strength sum rule is contributed by the plasmon mode and a negligible amount by the electron-hole pair excitations. Thus one expects a unique frequency ω to correspond to a particular wave vector k in Eq. (2.7). Then the integration over ω can be performed trivially, as B must be proportional to $\delta(\omega - \omega_k)$, where ω_k is the plasmon frequency. At short wavelengths the situation changes. One knows that the finite region of $\omega - k$ space corresponding to the electron-hole pair excitations contributes. This region is contained roughly in a band centered on the line $\omega = \hbar k^2/2m$ for large k. The important thing to recognize is that for large k the band is fairly narrow. Thus one can again attempt to approximate B by something proportional to $\delta(\omega - \omega_k)$, where ω_k now is an excitation resembling more a free particle than a plasmon. We therefore make the approximation of letting

$$B(\vec{k}, \omega) = \beta(\vec{k})\, \delta(\omega - \omega_k) \tag{2.8}$$

and

$$A(\vec{k}_\perp, \omega) = \alpha(\vec{k}_\perp)\, \delta(\omega - \sigma_{k_\perp}). \tag{2.9}$$

Since the surface properties are expected to be considerably different from bulk properties, an extra mode $\sigma_{k_\perp}$ has been introduced for them. Here β and α are amplitudes which will be specified shortly. Hence we find

$$\Phi(\vec{r}, t) = \int d^2k_\perp \int_0^\infty dk_z\, \beta(\vec{k}) \sin k_z z\, e^{i(\vec{k}_\perp\cdot\vec{r}-\omega_k t)} \Theta(-z) + \int d^2k_\perp\, \alpha(\vec{k}_\perp)\, e^{-k_\perp |z|}\, e^{i(\vec{k}_\perp\cdot\vec{r}-\sigma_{k_\perp} t)} + \text{c.c.} \tag{2.10}$$

The modes associated with the $\beta(\vec{k})$ amplitude permeate the volume of the crystal so will be called BQM. The modes associated with the $\alpha(k_\perp)$ amplitude are localized in the surface region so are termed SQM. As we will see later explicitly, the

BQM and SQM go over to bulk plasmons and surface plasmons in the long-wavelength limit.

We now quantize the fields associated with the BQM and SQM excitations. This is done by introducing creation and annihilation operators. Thus let

$$\beta(\vec{k}) = M_{\vec{k}}\, b_{\vec{k}} \tag{2.11}$$

and

$$\alpha(\vec{k}_\perp) = N_{\vec{k}_\perp}\, a_{\vec{k}_\perp} \ , \tag{2.12}$$

where $b_{\vec{k}}$ is an annihilation operator for the BQM and $a_{\vec{k}_\perp}$ is an annihilation operator for the SQM. Here M and N are normalization coefficients to be determined later. The SQM and BQM excitations are treated as bosons since we expect them to have a classical limit. Replacing the integrals by sums, via the standard replacements

$$\int d^3k \to \frac{(2\pi)^3}{V_c}\sum_{\vec{k}}$$

and

$$\int d^2k_\perp \to \frac{(2\pi)^2}{A}\sum_{\vec{k}_\perp} \ ,$$

we obtain the operator expansion for $\Phi(\vec{r}, t)$,

$$\Phi(\vec{r}, t) = \frac{(2\pi)^3}{V_c}\sum_{\vec{k}} [M_{\vec{k}}\, b_{\vec{k}} \sin k_z z\, e^{i(\vec{k}_\perp\cdot\vec{r}-\omega_k t)}\Theta(-z) + \text{H.c.}]$$

$$+\frac{(2\pi)^2}{A}\sum_{\vec{k}_\perp}[N_{\vec{k}_\perp}\, a_{\vec{k}_\perp}\, e^{-k_\perp|z|}\, e^{i(\vec{k}_\perp\cdot\vec{r}-\sigma_{\vec{k}_\perp}t)} + \text{H.c.}] \ . \tag{2.13}$$

Here V_c is the volume of the crystal and A is its area.

In summary, Eq. (2.13) is a mode expansion for the electrostatic potential. It is expressed in terms of four unknown functions $M_{\vec{k}}$, $N_{\vec{k}_\perp}$, $\omega_{\vec{k}}$, and $\sigma_{\vec{k}_\perp}$. In Sec. III and IV we will determine these in terms of the dielectric properties of the system.

III. COUPLING TO THE BULK QUASIMODES

The purpose of the present section is to determine the parameters $M_{\vec{k}}$ and $\omega_{\vec{k}}$ of Eq. (2.13). The result that we will obtain will correspond to the results of Overhauser, [1] but we repeat them here for two reasons. First of all, the method employed is quite different. It will admit a natural extension to the case of surface quasimodes to be considered in Sec. IV. Second, it perhaps is not obvious that the modes employed here, which are proportional to $\sin k_z z$, will produce the same coupling as the modes employed by Overhauser, which are proportional to $e^{ik_z z}$. The present derivation will also display the intimate connection existing between the analytic properties of the dielectric function and the oscillator strength sum rule.

We start by calculating the energy loss of moving test charge two ways. First we do it classically by calculating the work done by the medium on the charge as it moves through it. Then we evaluate the same quantity quantum mechanically by assuming that it radiates BQM waves as it traverses the medium. For simplicity's sake let us take the charge's location to be very deep in the medium so the coupling to SQM excitations may be neglected.

Thus, in the classical approach, one has essentially a charge moving through an infinite medium. Let the charge density be written as

$$\rho(\vec{r}, t) = Q\delta(\vec{r} - \vec{v}t) \ . \tag{3.1}$$

Expand the electrostatic potential in a Fourier series

$$\Phi(\vec{r}, t) = \int d\vec{k}\, d\omega\, e^{i(\vec{k}\cdot\vec{r}-\omega t)}\, \Phi(\vec{k}, \omega), \tag{3.2}$$

and similarly for the charge density

$$\rho(\vec{r}, t) = \int d\vec{k}\, d\omega\, e^{i(\vec{k}\cdot\vec{r}-\omega t)}\, \rho(\vec{k}, \omega) \ . \tag{3.3}$$

From the Poisson equation we have the relation

$$\Phi(\vec{k}, \omega) = \frac{4\pi}{k^2}\frac{\rho(\vec{k}, \omega)}{\epsilon(\vec{k}, \omega)} \ , \tag{3.4}$$

where

$$\rho(\vec{k}, \omega) = (Q/8\pi^3)\,\delta(\omega - \vec{k}\cdot\vec{v}) \tag{3.5}$$

Inserting Eqs. (3.4) and (3.5) into (3.2) yields

$$\Phi(\vec{r}, t) = \int d\vec{k}\, d\omega\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} \times [Q/2\pi^2 k^2 \epsilon(\vec{k}, \omega)]\,\delta(\omega - \vec{k}\cdot\vec{v}) \ . \tag{3.6}$$

The electric field is given by $\vec{E} = -\nabla\Phi$:

$$\vec{E}(\vec{r}, t) = \int d\vec{k}\, d\omega\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} \times Q\vec{k}/[2\pi^2 i k^2 \epsilon(\vec{k}, \omega)]\,\delta(\omega - \vec{k}\cdot\vec{v}) \ . \tag{3.7}$$

The electric field that would exist in the absence of a dielectric $\vec{E}^0$ would be obtained by setting $\epsilon(\vec{k}, \omega)$ equal to 1. Taking the difference of $\vec{E}$ and $\vec{E}^0$ gives the field due to the presence of the polarization charge. It is this field which does work on the charge Q as it progresses through the medium. Following Ritchie[7] we compute the work done on the charge,

$$\frac{dW}{dt} = Q(\vec{E} - \vec{E}^0)\big|_{\vec{r}=\vec{v}t}\cdot\vec{v} = \frac{Q^2}{\pi^2}\int d\vec{k}\int_0^\infty d\omega \times \frac{\omega}{k^2}\,\mathrm{Im}\frac{1}{\epsilon(\vec{k}, \omega)}\,\delta(\omega - \vec{k}\cdot\vec{v}) \ . \tag{3.8}$$

Here we have made use of the reality condition that $\epsilon(\vec{k}, \omega) = \epsilon^*(\vec{k}, -\omega)$.

The one-mode approximation is introduced at this stage. Let

$$\mathrm{Im}\frac{1}{\epsilon(\vec{k}, \omega)} = \Omega(\vec{k})\,\delta(\omega - \omega_k) \ . \tag{3.9}$$

Thus we assume that ϵ has a pole at $\omega = \omega_k$, where $\Omega(\vec{k})$ is related to the residue of the pole. The quantity $\Omega(\vec{k})$ will be determined later. Inserting Eq. (3.9) into Eq. (3.8) and performing the frequency integration leads to

$$\frac{dW}{dt} = \frac{Q^2}{\pi^2} \int d\vec{k} \frac{\omega_k}{k^2} \Omega(\vec{k}) \delta(\omega_k - \vec{k} \cdot \vec{v}) . \tag{3.10}$$

In order to obtain explicit formulas for ω_k and $\Omega(\vec{k})$ let us explore the analytic properties of the dielectric function. In particular, the function

$$f(\omega) = 1/\epsilon(\vec{k}, \omega) - 1 \tag{3.11}$$

has the property that $f(\omega) \to (\omega_p/\omega)^2$ as $\omega \to \infty$ since $\epsilon(\vec{k}, \omega) \to 1 - (\omega_p/\omega)^2$ in that limit. Here ω_p is the plasma frequency defined by $\omega_p^2 = 4\pi n e^2/m$, where n is the electronic density, and e and m refer to the charge and mass of the electron, respectively. It will be convenient to work in atomic units henceforth. Thus we will set $\hbar = 1$, $e = 1$, and $m = 1$. Energies will be measured in units of 27.2 eV and distances in units of Bohr radii, a_0. We find that $f(\omega)$ obeys the Kramers-Kronig dispersion relation

$$\mathrm{Re}\left(\frac{1}{\epsilon(\vec{k}, \omega_0)} - 1\right) = \frac{1}{\pi} \mathcal{P} \int_0^\infty d\omega \frac{2\omega}{\omega^2 - \omega_0^2} \mathrm{Im} \frac{1}{\epsilon(\vec{k}, \omega)} , \tag{3.12}$$

where $\mathcal{P}$ denotes the "principal part of."

Inserting the one-pole approximation of Eq. (3.9) into (3.12) leads to

$$\mathrm{Re}\,[1/\epsilon(\vec{k}, \omega) - 1] = (2/\pi)\,[\omega_k/(\omega_k^2 - \omega^2)]\,\Omega(\vec{k}) . \tag{3.13}$$

For very large values of ω the above equation reduces to

$$\omega_p^2 = -(2/\pi)\,\omega_k \Omega(\vec{k}) , \tag{3.14}$$

while for very small frequencies we find

$$1/\epsilon(\vec{k}, \omega) - 1 = 2\Omega(\vec{k})/\pi\omega_k . \tag{3.15}$$

Solving these for $\Omega(\vec{k})$ and ω_k yields

$$\omega_k = \omega_p \{\epsilon(\vec{k}, 0)/[\epsilon(\vec{k}, 0) - 1]\}^{1/2} , \tag{3.16}$$

and

$$\Omega(\vec{k}) = -\tfrac{1}{2}\pi\omega_p \{[\epsilon(\vec{k}, 0) - 1]/\epsilon(\vec{k}, 0)\}^{1/2} . \tag{3.17}$$

We observe that Eq. (3.16) is the same dispersion relation as obtained by Overhauser.[1] It provides us with an explicit formula for the BQM frequency in terms of the static dielectric function. For small wavelengths, $\epsilon \to \infty$, so $\omega_k \to \omega_p$. Thus the BQM reduces to a bulk plasmon in that limit. On the other hand, as $k \to \infty$, $\epsilon \to 1 + (2\omega_p/k^2)^2$ so $\omega_k \to \frac{1}{2}k^2$ which is just the free-electron dispersion relation.

Finally we evaluate the energy loss rate due to BQM emission quantum mechanically. Again let us assume the moving classical source to be deeply embedded in the crystal so that surface effects may be neglected. The interaction of this classical source with the quantized Φ field is

$$H_{\mathrm{int}} = \int d\vec{r}\, Q\delta(\vec{r} - \vec{R} - \vec{v}t) \frac{(2\pi)^3}{V_c} \times \sum_{\vec{k}} [M_k b_k \sin k_z z \Theta(-z) \times e^{i(\vec{k}_\perp \cdot \vec{r} - \omega_k t)} + \mathrm{H.c.}] . \tag{3.18}$$

From time-dependent perturbation theory one calculates the transition amplitude for this process:

$$C = (-i/\hbar) \int_{-\infty}^{\infty} dt \langle H_{\mathrm{int}} \rangle \tag{3.19}$$

where $\langle H_{\mathrm{int}} \rangle$ denotes a matrix element corresponding to BQM emission. Thus only the term associated with the creation operator contributes. To avoid any conceptual difficulty arising when $v_z \neq 0$, let us imagine $v_z = 0$ for this calculation. (This will guarantee that one need not worry about coupling to SQM modes at some stage of the t integration. It is clear that the result to be obtained won't depend on this assumption if we are deep enough in the crystal.) Then

$$C = (-2\pi i/\hbar)\, Q\delta(\omega_k - \vec{k}_\perp \cdot \vec{v}_\perp) \times [(2\pi)^3/V_c]\, M_k^* \sin k_z R_z \times e^{-i\vec{k}_\perp \cdot \vec{R}_\perp} . \tag{3.20}$$

Squaring the amplitude, multiplying by the energy of the quantum, $\hbar\omega_k$, and dividing by the duration of the experiment leads to an expression for the loss rate,

$$\frac{-dW}{dt} = \sum_{\vec{k}} \hbar\omega_{\vec{k}} \frac{\pi}{\hbar^2} Q^2 \delta(\omega_k - \vec{k}_\perp \cdot \vec{v}_\perp) \times [(2\pi)^6/V_c^2] |M_k|^2 . \tag{3.21}$$

Replacing the sum by an integral gives

$$\frac{-dW}{dt} = \int_{k_z \geq 0} d\vec{k} \frac{\pi\omega_k}{\hbar} Q^2 \delta(\omega_k - \vec{k}_\perp \cdot \vec{v}_{k_\perp}) \times [(2\pi)^3/V_c] |M_k|^2 . \tag{3.22}$$

Comparing this to the classical loss rate of Eq. (3.10) gives us an expression for $|M_k|^2$:

$$|M_k|^2 = \frac{-\hbar V_c \Omega(\vec{k})}{4\pi^6 k^2} = \frac{\hbar\omega_p V_c}{8\pi^5 k^2} \times \left(\frac{\epsilon(\vec{k}, 0) - 1}{\epsilon(\vec{k}, 0)}\right)^{1/2} . \tag{3.23}$$

This completes our task of computing the parameters of the BQM field. We note that a comparison of M_k with the coupling coefficient obtained by Overhauser leads to agreement within a numerical factor. This numerical factor is associated with the choice of $\sin k_z z$ rather than $e^{ik_z z}$.

In summary, we have shown that the analytic properties of the dielectric function, coupled with

the one-pole approximation, provide a powerful combination which allows us to determine the BQM field parameters in terms of the static dielectric function. In Sec. IV we apply the same set of techniques to the surface quasimodes.

IV. COUPLING TO SURFACE QUASIMODES

Let us now apply a similar approach to the study of the surface quasimodes. We begin by calculating the energy-loss rate for a particle due to its coupling with SQM waves. Then we study the analytic properties of the dielectric function associated with the SQM excitations. This is followed by a discussion of the quantum-mechanical calculation of the energy-loss rate.

Suppose we place an external test charge Q on the surface and allow it to only move on that plane. By definition, the BQM wave vanishes there, so we need only consider the coupling to SQM waves. Thus the external charge density assumes the form

$$\rho_{ex}(\vec{r}, t) = Q\delta(z)\,\delta^{(2)}(\vec{r}_\perp - \vec{v}_\perp t) \,. \tag{4.1}$$

Ritchie and Marusak[2] were able to obtain a dispersion relation for the surface plasmon by solving the following homogeneous problem. They considered an infinite dielectric medium and imagined a sheet of charge existing at the plane $z=0$. Since it was an infinite medium, the fields to the left or right of the $z=0$ plane could be expressed by simply using $\epsilon(\vec{k}, \omega)$, the infinite-medium dielectric function. Then they argued that if the surface had the property that it provided specular reflection for the electrons, one could replace the region $z>0$ by appropriate vacuum fields without altering the fields in the region $z<0$. We now make the same physical assumptions and solve the inhomogeneous problem of finding the fields induced by the charge density of Eq. (4.1). In computing the fields to the left of the surface we add what is in effect an image charge to ρ_{ex}. Rather than choose it as a point charge in the $z>0$ domain we treat it as a distributed charge in the $z=0$ plane. Thus we start by considering an infinite dielectric with charge density,

$$\rho(\vec{r}, t) = Q\delta(z)\,\delta^{(2)}(\vec{r}_\perp - \vec{v}_\perp t) + \delta(z)\,\sigma(\vec{r}_\perp, t) \,. \tag{4.2}$$

Expand the potential in a Fourier series similar to Eq. (3.2). From Poisson's equation it follows that

$$\Phi(\vec{k}, \omega) = [4\pi/k^2\epsilon(\vec{k}, \omega)] \times [(Q/8\pi^3)\,\delta(\omega - \vec{k}_\perp \cdot \vec{v}_\perp) + \sigma(\vec{k}_\perp, \omega)/2\pi] \,, \tag{4.3}$$

where

$$\sigma(\vec{k}_\perp, \omega) = \frac{1}{8\pi^3} \int d^2\vec{r}_\perp\, dt\, e^{-i(\vec{k}_\perp \cdot \vec{r} - \omega t)}\, \sigma(\vec{r}_\perp, t) \,. \tag{4.4}$$

Thus the potential is given by

$$\Phi(\vec{r}, t) = \int d\vec{k}\, d\omega\, \frac{4\pi}{k^2\epsilon(\vec{k}, \omega)} \times \left(\frac{Q}{8\pi^3}\,\delta(\omega - \vec{k}_\perp \cdot \vec{v}_\perp) + \frac{\sigma(\vec{k}_\perp, \omega)}{2\pi} \right) e^{i(\vec{k}\cdot\vec{r} - \omega t)} \,, \tag{4.5}$$

the electric field by

$$\vec{E}(\vec{r}, t) = \int d\vec{k}\, d\omega\, \frac{4\pi}{k^2\epsilon(\vec{k}, \omega)} \frac{\vec{k}}{i} \times \left(\frac{Q}{8\pi^3}\,\delta(\omega - \vec{k}_\perp \cdot \vec{v}_\perp) + \frac{\sigma(\vec{k}_\perp, \omega)}{2\pi} \right) e^{i(\vec{k}\cdot\vec{r} - \omega t)} \,, \tag{4.6}$$

and the electric displacement vector by

$$\vec{D}(\vec{r}, t) = \int d\vec{k}\, d\omega\, \frac{4\pi\vec{k}}{k^2 i} \times \left(\frac{Q}{8\pi^3}\,\delta(\omega - \vec{k}_\perp \cdot \vec{v}_\perp) + \frac{\sigma(\vec{k}_\perp, \omega)}{2\pi} \right) e^{i(\vec{k}\cdot\vec{r} - \omega t)} \,. \tag{4.7}$$

These are accepted as the solutions for $z<0$. In the $z>0$ region we now replace the crystal by a vacuum field and again assume specular reflection. Since $\nabla^2\Phi = 0$ it follows that

$$\Phi(\vec{r}, t) = \int d^2k_\perp\, d\omega\, e^{i(\vec{k}_\perp \cdot \vec{r} - \omega t)} \times A(\vec{k}_\perp, \omega)\, e^{-k_\perp z} \,, \tag{4.8}$$

and

$$\vec{E}(\vec{r}, t) = \vec{D}(\vec{r}, t) = \int d^2k_\perp\, e^{i(\vec{k}_\perp \cdot \vec{r} - \omega t)} \times A(\vec{k}_\perp, \omega)\, e^{-k_\perp z}(\vec{k}_\perp/i + k_\perp \hat{k}) \,. \tag{4.9}$$

The true external charge residing on the surface is given by

$$\sigma_{ex}(\vec{r}_\perp, t) = \int_{0-}^{0+} dz\, Q\delta(z)\,\delta^{(2)}(\vec{r}_\perp - \vec{v}_\perp t) = \frac{Q}{4\pi^2} \int e^{i(\vec{k}_\perp \cdot \vec{r} - \omega t)}\, \delta(\omega - \vec{k}_\perp \cdot \vec{v}_\perp) \times d^2k_\perp\, d\omega \,. \tag{4.10}$$

We now impose the boundary conditions that Φ be continuous across the boundary and that the jump in D_z be proportional to σ_{ex} via Gauss's law. Thus we obtain the following equations:

$$A(\vec{k}_\perp, \omega) = \int_{-\infty}^{-\infty} dk_z\, \frac{4\pi}{k^2\epsilon(\vec{k}, \omega)} \times \left(\frac{Q}{(2\pi)^3}\,\delta(\omega - \vec{k} \cdot \vec{v}) + \frac{\sigma(\vec{k}_\perp, \omega)}{2\pi} \right) , \tag{4.11}$$

and

$$k_\perp A(\vec{k}_\perp,\omega)-\int_{-\infty}^{\infty}dk_z\,e^{ik_z0^-}\left(\frac{4\pi k_z}{k^2 i}\right)\times\left(\frac{Q}{8\pi^3}\delta(\omega-\vec{k}_\perp\cdot\vec{v}_\perp)+\frac{\sigma(\vec{k}_\perp,\omega)}{2\pi}\right)=\frac{Q}{\pi}\delta(\omega-\vec{k}_\perp\cdot\vec{v}_\perp)\ . \tag{4.12}$$

Upon inserting the value of the following integral,

$$\int_{-\infty}^{\infty}\frac{dk_z}{k^2}\frac{k_z}{i}e^{ik_z0^-}=-\pi\ , \tag{4.13}$$

we find that

$$A(\vec{k}_\perp,\omega)=\frac{Q}{\pi k_\perp}\frac{\bar{\epsilon}(\vec{k}_\perp,\omega)}{1+\bar{\epsilon}(\vec{k}_\perp,\omega)}\times\delta(\omega-\vec{k}_\perp\cdot\vec{v}_\perp)\ , \tag{4.14}$$

and

$$\sigma(\vec{k}_\perp,\omega)=\frac{Q}{4\pi^2}\frac{1-\bar{\epsilon}(\vec{k}_\perp,\omega)}{1+\bar{\epsilon}(\vec{k}_\perp,\omega)}\times\delta(\omega-\vec{k}_\perp\cdot\vec{v}_\perp)\ , \tag{4.15}$$

where we have introduced the surface dielectric function $\bar{\epsilon}(\vec{k}_\perp,\omega)$ by defining

$$\bar{\epsilon}(\vec{k}_\perp,\omega)=\frac{k_\perp}{\pi}\int_{-\infty}^{\infty}dk_z\frac{1}{k^2\epsilon(\vec{k},\omega)}\ . \tag{4.16}$$

The surface-plasmon dispersion relation was found by Ritchie and Marusak[2] to be given by the solution to the equation

$$\bar{\epsilon}(\vec{k}_\perp,\omega)+1=0\ , \tag{4.17}$$

which yields an equation for ω as a function of $k_\perp$.

Having found expressions for the electric fields throughout all space, we now compute the work done by the medium per unit time on the test charge as it traverses the surface. As before, we calculate the difference between the electric fields in the presence and in the absence of a dielectric:

$$\vec{E}-\vec{E}^0=\int d^2k_\perp\,d\omega\,e^{i(\vec{k}_\perp\cdot\vec{r}-\omega t)-k_\perp z}\times\frac{Q}{2\pi k_\perp}\delta(\omega-\vec{k}_\perp\cdot\vec{v}_\perp)\left(\frac{2\bar{\epsilon}}{1+\bar{\epsilon}}-1\right)\times\left(\frac{\vec{k}_\perp}{i}+k_\perp\hat{k}\right)\Big|_{z=0^+}\ . \tag{4.18}$$

Here we have evaluated it at $z=0^+$. The same answer would be found if the calculation were made at $z=0^-$. Using the relation $\bar{\epsilon}(\vec{k}_\perp,-\omega)=\bar{\epsilon}^*(\vec{k}_\perp,\omega)$, we find the energy-loss rate to be

$$\frac{dW}{dt}=\int d^2k_\perp\int_0^\infty d\omega\frac{2\omega Q^2}{\pi k_\perp}\delta(\omega-\vec{k}_\perp\cdot\vec{v}_\perp)\times\mathrm{Im}\left(\frac{-1}{1+\bar{\epsilon}(\vec{k}_\perp,\omega)}\right)\ . \tag{4.19}$$

We now make the one-pole approximation for the SQM waves. Let

$$\mathrm{Im}\frac{1}{1+\bar{\epsilon}(\vec{k}_\perp,\omega)}\equiv\Lambda(\vec{k}_\perp)\,\delta(\omega-\sigma_{k_\perp})\ . \tag{4.20}$$

Then Eq. (4.19) becomes

$$\frac{dW}{dt}=-\int d^2k_\perp\frac{2\sigma_{k_\perp}Q^2}{\pi k_\perp}\times\delta(\sigma_{k_\perp}-\vec{k}_\perp\cdot\vec{v}_\perp)\Lambda(k_\perp)\ . \tag{4.21}$$

By exploring the analytic properties of $\bar{\epsilon}(\vec{k}_\perp,\omega)$ we hope to obtain explicit formulas for $\Lambda_{k_\perp}$, $\sigma_{k_\perp}$ and $N_{k_\perp}$. In our discussion of the BQM couplings we have developed an explicit expression for $1/\epsilon(\vec{k},\omega)$. Thus from Eqs. (3.9) and (3.13) it follows that

$$\frac{1}{\epsilon(\vec{k},\omega)}=1+2\omega_k\Omega(k)/\pi(\omega_k^2-\omega^2)+i\Omega(k)\,\delta(\omega-\omega_k)\ . \tag{4.22}$$

Hence we can write the surface dielectric function in the form

$$\bar{\epsilon}(\vec{k}_\perp,\omega)=1+\frac{k_\perp}{\pi}\int_{-\infty}^{\infty}\frac{dk_z}{k^2}\times\frac{2\omega_k\Omega(k)}{\pi(\omega_k+\omega)(\omega_k-\omega-i0^+)}\ . \tag{4.23}$$

Let us explore the analytic properties of this in the upper half-plane. Letting $\omega=\omega_1+i\omega_2$, we have

$$\mathrm{Im}\bar{\epsilon}(\vec{k}_\perp,\omega)=-\frac{k_\perp\omega_p^2}{\pi}\int_{-\infty}^{\infty}\frac{dk_z}{k^2}\times\frac{2\omega_1\omega_2}{(\omega_k^2-\omega_1^2+\omega_2^2)^2+4\omega_1^2\omega_2^2}\ . \tag{4.24}$$

Assume first that $\omega_1\neq0$. Then for $\omega_2\neq0$ the integral is nonzero so $\mathrm{Im}\bar{\epsilon}(\vec{k}_\perp,\omega)\neq0$. Hence $1/[1+\bar{\epsilon}(\vec{k}_\perp,\omega)]$ has no poles in the upper half-plane. The case where $\omega_1=0$ needs to be treated separately since $\mathrm{Im}\bar{\epsilon}$ does vanish. However, we note that

$$\bar{\epsilon}(\vec{k}_\perp,\omega)=1-\frac{k_\perp^2\omega_p^2}{\pi}\int_{-\infty}^{\infty}\frac{dk_z}{k^2}\frac{1}{\omega_2^2+\omega_k^2}\geq1-\frac{k_\perp\omega_p^2}{\pi}\int_{-\infty}^{\infty}\frac{dk_z}{k^2}\frac{1}{\omega_k^2}\ . \tag{4.25}$$

Since $\omega_k=\omega_p[\epsilon/(\epsilon-1)]^{1/2}$ and $\epsilon>0$ it follows that $\omega_k>\omega_p$. It follows that

$$\bar{\epsilon}(\vec{k}_\perp,\omega)\geq1-\frac{\omega_p^2k_\perp}{\pi}\int_{-\infty}^{\infty}\frac{dk_z}{k^2}\frac{1}{\omega_p^2}=0\ , \tag{4.26}$$

so $\bar{\epsilon}$ cannot be equal to -1. Thus we conclude that $\bar{\epsilon}(\vec{k}_\perp,\omega)$ is analytic in the upper half-ω-plane. This could alternatively been deduced from the standard causality argument which states that the response of the system to a pulse of surface plasmons cannot precede the arrival of that pulse.

The function

$$f(\omega) = 1/[1 + \bar{\epsilon}(\vec{k}_\perp, \omega)] - \tfrac{1}{2} \tag{4.27}$$

is analytic in the upper half-plane. As $\omega \to \infty$ the dielectric function $\epsilon \to 1 - \omega_p^2/\omega^2$, so it follows from Eq. (4.16) that $\bar{\epsilon} \to 1 + \omega_p^2/\omega^2$. Hence f falls off quadratically with ω for large ω. The Kramers-Kronig relation for $f(\omega)$ yields

$$\mathrm{Re}\left(\frac{1}{1+\bar{\epsilon}(\vec{k}_\perp, \omega_0)} - \frac{1}{2}\right) = \frac{1}{\pi} \mathcal{P} \int_0^\infty d\omega \times \frac{2\omega}{\omega^2 - \omega_0^2} \mathrm{Im} \frac{1}{1+\bar{\epsilon}(\vec{k}_\perp, \omega)} . \tag{4.28}$$

Inserting the one-pole approximation into the above equation gives

$$\mathrm{Re}\left(\frac{1}{1+\bar{\epsilon}(\vec{k}_\perp, \omega_0)} - \frac{1}{2}\right) = -\frac{2}{\pi} \sigma_{k_\perp} \times \frac{\Lambda(k_\perp)}{\omega_0^2 - \sigma_{k_\perp}^2} . \tag{4.29}$$

This equation is evaluated in the high-frequency limit and in the low-frequency limit and the following expressions for Λ and σ are obtained:

$$\Lambda(k_\perp) = \pi \omega_p \tfrac{1}{8} \sqrt{2} \left(\frac{1 - \bar{\epsilon}(\vec{k}_\perp, 0)}{1 + \bar{\epsilon}(\vec{k}_\perp, 0)}\right)^{1/2} \tag{4.30}$$

and

$$\sigma_{k_\perp} = \frac{\omega_p}{\sqrt{2}} \left(\frac{1 + \bar{\epsilon}(\vec{k}_\perp, 0)}{1 - \bar{\epsilon}(\vec{k}_\perp, 0)}\right)^{1/2} . \tag{4.31}$$

Thus Λ and σ depend on $\bar{\epsilon}(\vec{k}_\perp, 0)$ which, in turn, depends only on $\epsilon(\vec{k}, 0)$, through the relation

$$\bar{\epsilon}(\vec{k}_\perp, 0) = (k_\perp/\pi) \times \int_{-\infty}^{\infty} [dk_z / k^2 \epsilon(\vec{k}, 0)] . \tag{4.32}$$

It is instructive to examine the limiting cases of Eq. (4.32). For small $k_\perp$ we note that

$$\lim_{k_\perp \to 0} \frac{k_\perp}{\pi} \frac{1}{k_\perp^2 + k_z^2} = \delta(k_z) , \tag{4.33}$$

so

$$\lim_{k_\perp \to 0} \bar{\epsilon}(\vec{k}_\perp, 0) = \int_{-\infty}^{\infty} dk_z \, \delta(k_z) \times \frac{1}{\epsilon(k_z, 0)} = 0 . \tag{4.34}$$

Hence, from Eq. (4.31), it follows that $\sigma_{k_\perp} \to \omega_p/\sqrt{2}$ in this limit, which is just the long-wavelength limit of the surface-plasmon dispersion formula (excluding retardation effects). For large $k_\perp$ we have

$$\bar{\epsilon}(\vec{k}_\perp, 0) \Rightarrow \frac{k_\perp}{\pi} \int_{-\infty}^{\infty} \frac{dk_z}{k^2} \times \left[1 + \left(\frac{2\omega_p}{k^2}\right)^2\right]^{-1} = 1 - \frac{3}{8}\left(\frac{2\omega_p}{k_\perp^2}\right)^2 . \tag{4.35}$$

Hence the SQM frequency goes asymptotically to

$$\sigma_{k_\perp} \to k_\perp^2 \sqrt{\tfrac{2}{3}} . \tag{4.36}$$

This differs from the result obtained for the BQM made in that it is not a free-electron dispersion relation. However, we may perhaps be willing to accept that because, in reality, the SQM wave is constrained to ride along the surface. In fact, a sum over all k_z is involved in generating the surface dielectric function, and hence the SQM wave, as is seen from Eq. (4.32).

Let us now calculate the loss rate due to emission of SQM excitations. The interaction with the classical source is described by the Hamiltonian

$$H_{\mathrm{int}} = \int \rho(\vec{r}, t) \Phi_{\mathrm{SQM}}(\vec{r}, t) \, d\vec{r} , \tag{4.37}$$

where only the SQM part of Eq. (2.13) contributes. Taking matrix elements between a no-SQM state and a one-SQM state gives

$$\langle H_{\mathrm{int}} \rangle = \int d\vec{r} \, Q \delta^{(2)}(\vec{r}_\perp - \vec{v}_\perp t) \times \delta(z) \, [(2\pi)^2/A] \times N_{k_\perp}^* \, e^{-k_\perp |z|} \, e^{-i(\vec{k}_\perp \cdot \vec{r} - \sigma_{k_\perp} t)} . \tag{4.38}$$

Evaluating the energy-loss rate, as before, we find

$$\frac{dW}{dt} = -Q^2 \int d^2 k_\perp \, \sigma_{k_\perp} \frac{(2\pi)^3}{\hbar A} \times |N_{k_\perp}|^2 \, \delta(\vec{k}_\perp \cdot \vec{v}_\perp - \sigma_{k_\perp}) . \tag{4.39}$$

Finally, comparing this with the classical expression, Eq. (4.21) gives

$$|N_{k_\perp}|^2 = \frac{A}{4\pi^4 k_\perp} \Lambda(k_\perp) . \tag{4.40}$$

Thus the task of expressing the various parameters in terms of the static dielectric function has been completed.

V. OPTICAL POTENTIAL

In nuclear physics[8] it is customary to describe the scattering of nucleons from nuclei by means of a complex energy-dependent space-dependent (and sometimes even nonlocal) optical potential. The imaginary part of the potential takes into account the inelastic processes that can occur, such as absorption of nucleons by the nucleus. The concept of the optical potential can be adopted for use in solids without much change. We start by examining the Schrödinger equation in the presence of such a potential:

$$\left(-\tfrac{1}{2}\nabla^2 + V - iU - i\frac{\partial}{\partial t}\right)\Psi = 0 . \tag{5.1}$$

The particle density is given by $n=\Psi^*\Psi$ and the particle current density by $\vec{J}=-\frac{1}{2}i(\Psi^*\nabla\Psi-\Psi\nabla\Psi^*)$. Then one derives the continuity equation

$$\nabla\cdot\vec{J}+\frac{\partial n}{\partial t}=-2Un\ . \tag{5.2}$$

Thus we interpret $2U$ as the loss rate, or alternatively as the transition rate. In the present section, for the sake of simplicity, we will treat U as being a local potential. This assumption is usually quite valid as long as resonances are absent.

The loss rate of a particle moving parallel to the surface will be calculated by treating it as a classical source coupled to a quantized field. By comparing the loss rate thus obtained with Eq. (5.2) we will find explicit formulas for the optical potential. We note that there are several complicating factors that arise in deducing the optical potentials. First of all the optical potential can be expected to depend on the orientation of the velocity vector relative to the normal to the surface. We will neglect this variation in the present treatment. Preliminary estimates of the optical potential[4] have shown this variation to be rather insignificant. Second, since we are working with a classical source that moves at fixed speed through space, the optical potentials are going to depend on the speed rather than on the energy. Thus one expects the optical potential to be dependent, to some extent, on the crystalline potential V. This dependence will usually be quite small, however.

The cases of motion in the vacuum and motion within the crystal will be treated separately. In the vacuum region ($z>0$) there is only coupling to the SQM waves. The test charge is of the form

$$\rho=-\delta(z-\xi)\,\delta^{(2)}(\vec{r}_\perp-\vec{v}_\perp t)\ . \tag{5.3}$$

Thus the interaction Hamiltonian is

$$H_{\rm int}=\int\rho\Phi_{\rm SQM}\,d\vec{r}\ . \tag{5.4}$$

The square of the transition amplitude is proportional to the transition rate R, so we find

$$R=\sum_{k_\perp}\frac{(2\pi)^5}{A^2}\,|N_{k_\perp}|^2\,e^{-2k_\perp|\xi|}\,\delta(\vec{k}_\perp\cdot\vec{v}_\perp-\sigma_{k_\perp}). \tag{5.5}$$

Equating this with $2U$ gives us an expression for the optical potential for $\xi>0$:

$$U=\frac{4\pi^3}{A}\int d^2k_\perp\,|N_{k_\perp}|^2\,e^{-2k_\perp\xi}\delta(\sigma_{k_\perp}-\vec{k}_\perp\cdot\vec{v}). \tag{5.6}$$

Next let us analyze the case where the probing charge is inside the crystal, so both BQM and SQM modes have to be considered. The optical potential is expressed as the sum of two contributions:

$$U=U_1+U_2\ , \tag{5.7}$$

where U_1, the contribution from the SQMs, is given by

$$U_1=\frac{4\pi^3}{A}\int d^2k_\perp\,|N_{k_\perp}|^2\,e^{+2k_\perp\xi}\times\delta(\sigma_{k_\perp}-\vec{k}_\perp\cdot\vec{v})\ . \tag{5.8}$$

The BQM contribution U_2 is obtained by evaluating the matrix elements to

$$H_{\rm int}=\int\rho\Phi_{\rm BQM}\,d\vec{r}\ . \tag{5.9}$$

The transition amplitude is

$$C=i\frac{(2\pi)^4}{V_c}M_k^*\sin k_z\xi\times\delta(\omega_k-\vec{k}\cdot\vec{v})\ , \tag{5.10}$$

Proceeding with the evaluation of the transition rate, we find

$$2U_2=R=[(2\pi)^4/V_c]\int d^2k_\perp\int_0^\infty dk_z\,|M_k|^2\times\sin^2k_z\xi\,\delta(\omega_k-\vec{k}_\perp\cdot\vec{v})\ . \tag{5.11}$$

Hence the final expression for the optical potential is

$$U=\frac{8\pi^4}{V_c}\int d^2k_\perp\int_0^\infty dk_z\,|M_k|^2\sin^2k_zz\times\delta(\omega_k-\vec{k}_\perp\cdot\vec{v})\,\Theta(-z)+\frac{4\pi^3}{A}\int d^2k_\perp\,|N_{k_\perp}|^2\,e^{-2k_\perp|z|}\times\delta(\sigma_{k_\perp}-\vec{k}_\perp\cdot\vec{v})\ . \tag{5.12}$$

The azimuthal integrations may be performed by noting that

$$\int_0^{2\pi}d\phi\,\delta(\omega-kv\cos\phi)=2\frac{\Theta(kv-\omega)}{(k^2v^2-\omega^2)^{1/2}} \tag{5.13}$$

In the first integral a further reduction can be made by noticing that $k=(k_\perp^2+k_z^2)^{1/2}$, so

$$\int_0^\infty dk_\perp\,k_\perp\int_0^\infty dk_z\cdots=\int_0^\infty dk\,k\int_0^k dk_z\cdots$$

and

$$\int_0^k dk_z\,\frac{\sin^2k_zz}{(k^2v^2-\omega_k^2)^{1/2}}=\frac{\pi\Theta(kv-\omega_k)}{4v}\times\left(1-J_0\left\{2z\left[k^2-\left(\frac{\omega_k}{v}\right)^2\right]^{1/2}\right\}\right). \tag{5.14}$$

Express the potential as the sum of a bulk part U_B and a surface part U_S:

$$U=U_B+U_S\ , \tag{5.15}$$

where

$$U_B = \frac{\omega_p^2}{2v}\int_{k_1}^{k_2}\frac{dk}{k\omega_k} \times\left(1 - J_0\left\{2z\left[k^2 - \left(\frac{\omega_k}{v}\right)^2\right]^{1/2}\right\}\right)\Theta(-z)\,, \tag{5.16}$$

and

$$U_S = \frac{\omega_p^2}{4v}\int_{k_{\perp_1}}^{k_{\perp_2}}\frac{dk_\perp}{\sigma_{k_\perp}} \times\frac{e^{-2k_\perp|z|}}{[k_\perp^2 - (\sigma_{k_\perp}/v)^2]^{1/2}}\,. \tag{5.17}$$

Here k_1 and k_2 refer to the lower and higher roots of the equation $\omega_k = kv$, and $k_{\perp_1}$ and $k_{\perp_2}$ are the corresponding roots to $\sigma_{k_\perp} = k_\perp v$. The present results represent a significant generalization of previous calculations[4] in that the spatial dependence of the optical potentials is now explicitly displayed. Equations (5.16) and (5.17) are one-dimensional integrals describing the optical potentials and can be generated without much difficulty.

The limiting cases for the optical potentials are of some interest. For $z \to -\infty$, i.e., deep in the crystal, we can neglect the Bessel function and find

$$U_B \xrightarrow[z\to-\infty]{} (\omega_p^2/2v)\int_{k_1}^{k_2} dk/k\omega_k\,. \tag{5.18}$$

Thus U_B approaches a constant value deep in the crystal. Near the surface there is some small oscillatory behavior associated with the Bessel function of Eq. (5.16).

An approximate formula for U_S can be found for large z which explicitly shows that the surface contribution falls off rapidly as one goes away from the surface region. Since the exponential is a rapidly decreasing function of k, in Eq. (5.17), it follows that the major contribution to the integral arises from the region $k_\perp = k_{\perp_1}$. Thus

$$U_S \approx \frac{\omega_p^2}{4v}\frac{1}{\sigma_{k_\perp}(2k_{\perp_1})^{1/2}} \times\int_{k_{\perp_1}}^{\infty} dk_\perp \frac{e^{-2k_\perp|z|}}{(k_\perp - k_{\perp_1})^{1/2}}\,, \tag{5.19}$$

where the upper limit has been extended to infinity. Thus we obtain the asymptotic formula:

$$U_S \xrightarrow[|z|\to\infty]{} \frac{\omega_p^2\,\pi^{1/2}\,e^{-2k_{\perp_1}|z|}}{8v^2 k_{\perp_1}^{3/2}|z|^{1/2}}\,. \tag{5.20}$$

In model calculations it will be convenient to idealize the optical potential and wash over the small-scale oscillations that appear in $U(z)$. The potential can be treated as being more or less constant within the crystal. Superimposed on this bulk contribution is a rather intense spike located in the vicinity of the surface. This spike originates mainly from the coupling to surface plasmons, which are highly localized in the vicinity of the surface. In the most general case we idealize U in the form

$$U = \gamma(E)\Theta(-z) + \beta(E)\,\delta(z)\,. \tag{5.21}$$

We can obtain analytic formulas for $\gamma(E)$ and $\beta(E)$ by matching the Fourier components of Eq. (5.21) with the Fourier components of the more exact Eq. (5.15) at low and high wave vectors. Thus

$$\int_{-\infty}^{\infty} U e^{ipz}\,dz = \beta + \gamma\int_{-\infty}^{\infty} dz\,\Theta(-z)\,e^{ipz}\,. \tag{5.22}$$

For $p = 0$ both sides diverge. The coefficients of the divergent terms must match so we find that

$$\gamma = (\omega_p^2/2v)\int_{k_1}^{k_2} dk/k\omega_k\,. \tag{5.23}$$

Now let us look at Eq. (5.22) for high-p values:

$$\int_{-\infty}^{\infty} U_B\,e^{ipz}\,dz = \int_{-\infty}^{0} dz\,e^{ipz}\,\frac{\omega_p^2}{2v}\int_{k_1}^{k_2}\frac{dk}{k\omega_k} \times\left(1 - J_0\left\{2z\left[k^2 - \left(\frac{\omega_k}{v^2}\right)^2\right]^{1/2}\right\}\right) \tag{5.24}$$

and

$$\int_{-\infty}^{\infty} U_S\,e^{ipz}\,dz = \int_{-\infty}^{\infty} dz\,e^{ipz} \times\frac{\omega_p^2}{4v}\int_{k_{\perp_1}}^{k_{\perp_1}}\frac{dk_\perp}{\sigma_{k_\perp}}\,\frac{e^{-2k_\perp|z|}}{[k_\perp^2 - (\sigma_{k_\perp}/v)^2]^{1/2}}\,. \tag{5.25}$$

Imagine integrating each term by parts to develop an asymptotic expansion in powers of $1/p$. Then only the function and its derivatives in the neighborhood of $z = 0$ will matter. Notice that U_S is more discontinuous than U_B in this vicinity. The U_S function has a discontinuous first derivative while the U_B function has a discontinuous second derivative. Thus one expects U_S to dominate the high-p behavior of the Fourier transforms. The effect of U_B will be neglected and we find

$$\beta = \int_{-\infty}^{\infty} U_S\,e^{ipz}\,dz = \frac{\omega_p^2}{4v}\int_{k_{\perp_1}}^{k_{\perp_2}}\frac{dk}{\sigma\mu} \times\frac{1}{k^2 - (\sigma_{k_\perp}/v)^2}\,\frac{4k_\perp}{p^2 + 4k_\perp^2}\,. \tag{5.26}$$

In actually evaluating β we will take $p = v$.

In some instances the effect of the surface-plasmon contribution is found to compensate for the depression of the bulk-plasmon contribution near the surface. Then it is clear that a model in which $\beta = 0$ is adequate. However, below the threshold for BQM emission, the β term cannot be neglected.

In the present treatment of the optical potential

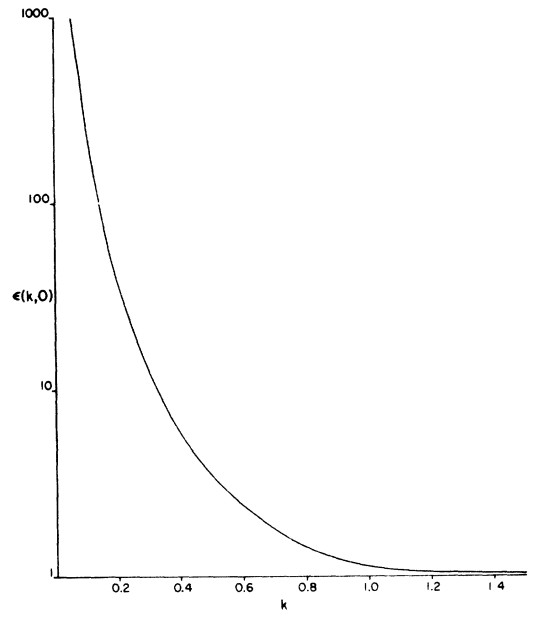

FIG. 1. Bulk dielectric function $\epsilon(\vec{k}, 0)$ plotted as a function of wave number k for potassium. All quantities are expressed in terms of atomic units.

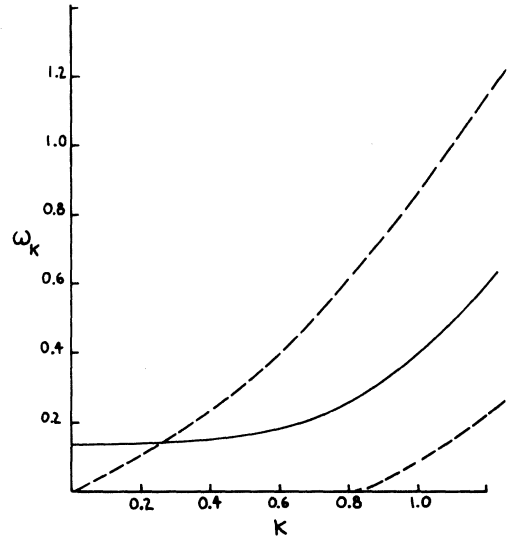

FIG. 3. Bulk quasimode dispersion curve giving the angular frequency ω_k as a function of the wave number k. The dashed curves represent the boundaries of the domain of electron-hole-loss excitations. The curve is for potassium.

we have neglected any real optical potential which might be present and considered only an imaginary term. In principle such a term does exist, although one expects that it would be small compared to the crystalline potential.

VI. RESULTS AND DISCUSSION

In Secs. I–V formulas were obtained for the dispersion relations, coupling parameters, and optical potentials associated with bulk and surface excitations in the crystal. Let us now compute these for a specific material. Since in subsequent papers we will be interested in studying photoemission in the alkali metals, we do the computation for potassium. We have found that all the parameters of interest can be calculated if the static dielectric function is specified. Overhauser[1] has formulated an expression for the dielectric function which takes into account exchange and correlation effects and which agrees with the detailed many-body calculations of the ground-state energy of metals. We adopt this dielectric function in the present section.

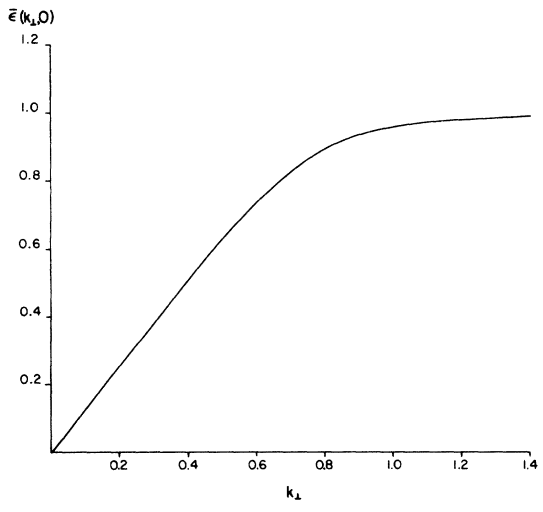

FIG. 2. Surface dielectric function $\bar{\epsilon}(\vec{k}_\perp, 0)$ plotted as a function of transverse wave numbers $k_\perp$ for potassium.

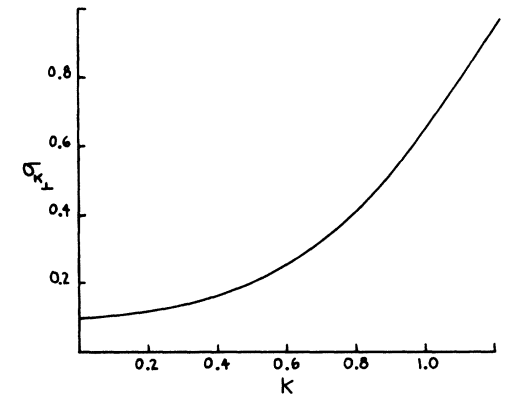

FIG. 4. Surface-quasimode-dispersion curve giving the angular frequency $\sigma_{k_\perp}$ as a function of the transverse wave number $k_\perp$. The curve is for potassium.

Thus we let

$$\epsilon(\vec{q},0)=1+Q(x)/[1-G(x)\,Q(x)]\,, \tag{6.1}$$

where $x=q/2k_F$, k_F being the Fermi wave-number. Here

$$Q(x)=\frac{1}{\pi k_F}\frac{1}{x^2}\left(\frac{1}{2}+\frac{1-x^2}{4x}\ln\left|\frac{1-x}{1+x}\right|\right). \tag{6.2}$$

and

$$G(x)=\frac{1.1x^2}{(1+10x^2+1.5x^4)^{1/2}}\,. \tag{6.3}$$

The parameters which were employed in the present calculation are $\epsilon_F=2.1$ eV and $\hbar\omega_p=3.7$ eV.

In Fig. 1 we present the dielectric function $\epsilon(\vec{k},0)$ for potassium. As expected, it gets to be large and positive for small wave numbers and approaches unity at large wave numbers, the approach being a monotomic one. In Fig. 2 the surface dielectric function of Eq. (4.16) is presented for potassium. In doing the integral it was convenient to let $k_z=k_\perp\tan\theta$ and to do the integration over the θ variable. At low wave number, $\bar{\epsilon}$ goes to zero linearly with $k_\perp$. At high wave numbers, $\bar{\epsilon}$ approaches the free-space value of unity.

The dispersion formula for the BQM excitations is presented in Fig. 3. For small k it lies close to the bulk-plasmon curve but is not identical to it for finite k. At large k it approaches the free-particle dispersion curve. The dashed lines illustrate the boundaries of the domain of electron-hole pair excitation. In Fig. 4 the corresponding dispersion curve for the SQM waves is presented.[9] Here again we note a transition from surface-plasmon-like behavior at small transverse wave numbers to something quite different at large k.

In Fig. 5 the bulk optical potential as computed from Eq. (5.16) is presented for several values of the speed v. We notice that, as expected, the bulk optical potential vanishes at $z=0$. The size of the characteristic oscillations are indeed observed to be small, thereby justifying their neglect in model calculations. Figure 6 displays the surface optical potential U_S for a couple of speeds. One notes that the spike is rather sharp indeed. Again, this points to the fact that the main coupling to the surface plasmons occurs as the particle crosses the surface. The explanation for this phenomenon has been given elsewhere.[4] As long as the charged particle is outside of the surface region the surface tries to remain an equipotential. Hence the field lines are normal to the surface and the coupling between the charge and the surface fluctuations is weak. When the particle is on the surface, however, its field lines radiate through the plane of the surface and the coupling gets to be anomalously large. Of course dynamic screening effects modify this static picture somewhat, but Fig. 6

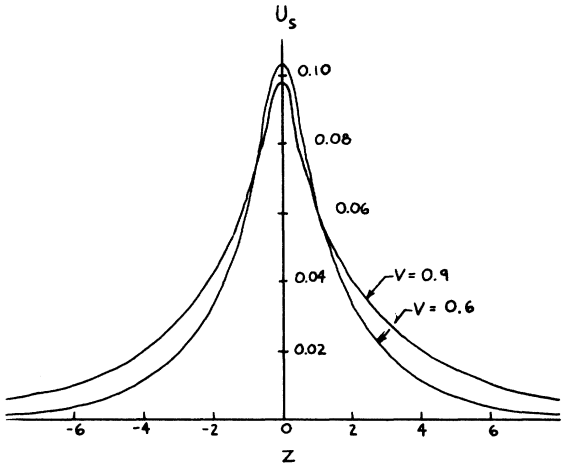

FIG. 6. Surface optical potential U_S plotted as a function of distance perpendicular to the surface z. Curves are presented for potassium for two values of the speed v.

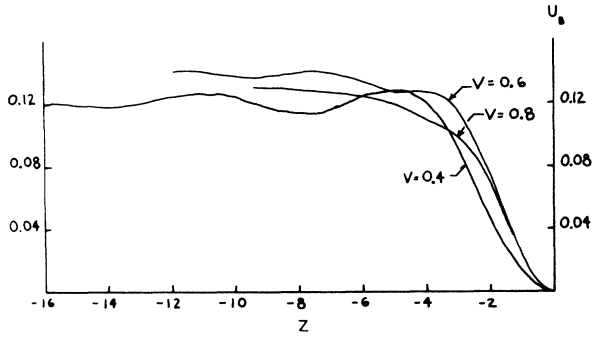

FIG. 5. Bulk optical potential U_B plotted as a function of distance into the crystal z for potassium. Curves are given for several particle speeds v.

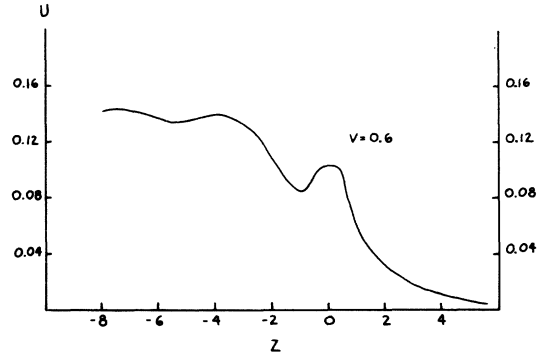

FIG. 7. Total optical potential U as a function of distance for a speed of $v=0.6$ for potassium.

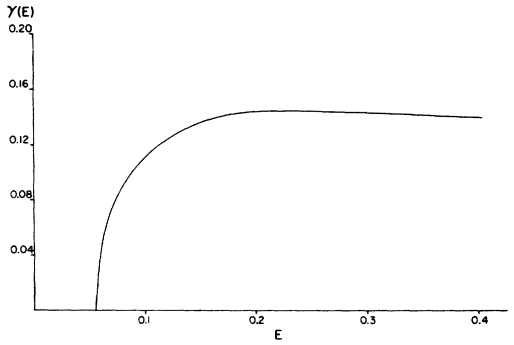

FIG. 8. Coefficient $\gamma(E)$, associated with the bulk optical potential, as a function of energy E for potassium.

shows that essentially this argument is valid. In Fig. 7 the total optical potential is given for a particular value of v. We notice that the effect of U_S is to fill in the depression of U_B near the surface, to a large extent.

The function $\gamma(E)$ of Eq. (5.23) is plotted as a function of energy $E = \frac{1}{2}v^2$ in Fig. 8. The existence of the threshold may be understood by remembering the definition of k_1 and k_2 of Eq. (5.23). For v sufficiently small, the line kv does not intersect the ω_k curve for any value of k, so no absorption occurs. Physically this means that it is energetically impossible for the particle to emit a BQM excitation. In reality we would expect the threshold to lie at the Fermi surface and not at a higher energy. For small energies one always has the possibility of exciting low momentum electron hole pairs. The oscillator strength associated with such excitation, however are very small, because at these momenta the bulk plasmons are saturating the sum rule. Hence it is quite reasonable to neglect such losses altogether until it is energetically possible for either a BQM or bulk plasmon to be emitted. It should be noted that the variation of $\gamma(E)$ with energy is practically constant once one has passed the threshold region. It does fall off rather slowly at higher energies. This behavior is consistent with other studies made of hot-electron lifetimes in metals.

In summary the goal of this paper has been to show how a one-electron Hamiltonian such as

$$H_0 = -\tfrac{1}{2}\nabla^2 + V + H_{\text{per}} \tag{6.4}$$

can be generalized to include some many-body effects. This is accomplished by adding to H_0 some additional terms:

$$H = H_0 - iU - \Phi + \sum_k \omega_k (b_k^\dagger b_k + \tfrac{1}{2}) + \sum_{k_\perp} \sigma_{k_\perp} (a_{k_\perp}^\dagger a_{k_\perp} + \tfrac{1}{2}) \,. \tag{6.5}$$

Here U represents the optical potential and is given by Eqs. (5.15)–(5.17), Φ is the coupling to the quasimode excitations and is given by Eq. (2.13), and the other terms correspond to the free BQM and SQM fields. One then proceeds to include many-body effects by working to various orders in perturbation theory. This will be done for photoemission in the following paper.

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[1]A. W. Overhauser, Phys. Rev. B **3**, 1883 (1971).
[2]R. H. Ritchie and A. L. Marusak, Surf. Sci. **4**, 234 (1966).
[3]D. E. Beck, Phys. Rev. A 4, 1555 (1971); R. H. Ritchie, Prog. Theor. Phys. 29, 607 (1963); Wagner, Z. Naturforsch. A 21, 634 (1966).
[4]J. I. Gersten, Phys. Rev. **188**, 774 (1969); Phys. Rev. B **2**, 3457 (1970).
[5]R. A. Ferrell, Phys. Rev. **107**, 450 (1957); H. Raether, Ergeb. Exakten Naturwiss. **38**, 84 (1965).
[6]P. Nozières and D. Pines, Nuovo Cimento **9**, 470 (1958).
[7]R. H. Ritchie, Phys. Rev. **106**, 874 (1957).
[8]H. Feshbach, C. E. Porter, and V. F. Weisskopf, Phys. Rev. **96**, 448 (1954); J. J Quinn, Phys. Rev. **126**, 1453 (1962); J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).
[9]Similar calculations for other materials have been made in Ref. 2.