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Theory of bulk and surface photoeffects in a free-electron metal

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In order to obtain new, general, conceptual insight into some aspects of the theory of photoemission, a consistent treatment was developed for photoemission from a free-electron (FE) metal with vanishingly small absorption at photon energies larger than the bulk-plasmon excitation energy. The electromagnetic response of the FE metal was described by the dielectric function $\epsilon(\vec{q},\omega)$ derived by Melnyk and Harrison. Calculated photoelectron energy-distribution curves (EDC) differ significantly both in magnitude and dependence on photon energy from the conventional FE results. The wave-vector selection rule for photoemission from a semi-infinite FE solid was derived. The separation of bulk and surface contributions to photoemission and its relation to "direct" and "nondirect" electronic transitions are reexamined and shown to be less reliable than commonly assumed. A new bulk contribution to the photoemitted current is identified and is associated with transitions which do not conserve the component of momentum normal to the surface. These "direct-like" transitions are shown to be closely related to ordinary direct (bulk) transitions; their occurrence is independent of an explicit electron-electron or electron-phonon interaction, and is not necessarily related to a finite extraction depth of the electrons. A bulk enhancement of the classical surface photoeffect associated with the gradient of the surface barrier is also identified. The vectorial effect is shown not to discriminate between surface and bulk photoeffects. For *p*-polarized photons the EDC is shown to depend strongly on the photon angle of incidence. The photoyield is shown to exhibit a sharp peak at the critical angle for total reflection. In contrast to earlier calculations, our calculation of the high photon-energy limit of the photoelectric yield from the FE metal agrees with the asymptotic yield from an atom.

I. INTRODUCTION

This is the first of a series of papers whose purpose is to provide general qualitative insight into the theory of photoemission. This can be achieved by considering relatively simple models which permit a more complete formal analysis than the more complex models which require a primarily numerical analysis. In the present paper we concentrate on the rather subtle relation between bulk and surface photoemission. The derivation and elucidation of the wave-vector selection rule for bulk photoemission from semi-infinite solids is one of the more interesting new results obtained.

The separation of surface from bulk effects is a central and long-standing problem in the analysis of photoemission data. Much of the current qualitative understanding of this problem is based on the free-electron (FE) model of a semi-infinite metal. In the simplest version of the model the surface barrier, confining the electrons in the metal, is represented by a step-function discontinuity in the potential. This FE model has been applied in the theory of photoemission by Fowler,[1] Mitchell,[2] and others.[3–5] In all of these theories, photoemission from a free-electron metal was considered to be an example of a pure surface photoeffect. This conclusion, and more generally, one of the current theoretical interpretations of the surface photoeffect rests on the following operator identity:

$$\frac{d}{dt}\vec{p}_{\rm op} = -\vec{\nabla} V_{\rm op} \ .$$

Applying this identity in a transformation of the matrix element for photoexcitation, in the approximation of a spatially constant vector potential, the photoemitted current is seen to exhibit a contribution proportional to the gradient of the surface potential. This contribution to the photoemitted current has been conventionally identified as the surface photoeffect. In the simple model of a free-electron metal considered by Mitchell[2] and Adawi[5] this represented the entire photoeffect. We shall show that the matrix element for photoexcitation can be evaluated directly and that it differs from the transformed matrix element. Part of this discrepancy is readily interpreted as a bulk contribution to the photocurrent. This result demonstrates directly that

photoemission from a free-electron metal cannot be viewed as a pure surface effect. In particular, in the limit of a vanishingly small photon-absorption probability we find a contribution to the energy-distribution curve (EDC) of the photoelectrons which is closely related to the "direct," i.e., momentum-conserving, transitions which cannot occur in the FE model. The physical reason for the difference between our analysis and other free-electron analyses such as the classical work of Mitchell[2] and other more elegant reformulations of this model[5-7] is that we required the photon flux transmitted into the semi-infinite solid to be completely absorbed:

$$\lim_{z\to-\infty}\vec{A}(\vec{r})=0\ .$$

This physical constraint must be satisfied even in the limit of a vanishingly small absorption coefficient which occurs at photon energies above the plasmon-excitation energy. This implies that we should no longer apply the approximation

$$\langle f\,|\,\vec{A}\cdot\vec{p}\,|\,i\rangle\approx\vec{A}\cdot\langle f\,|\,\vec{p}\,|\,i\rangle$$

$$=\frac{i\hbar\vec{A}}{\omega_{fi}}\cdot\langle f\,|\,\vec{\nabla}V\,|\,i\rangle\ .$$

This conclusion has also been previously reached for a totally different reason by authors[4,8-10] considering the rapid spatial variation of the vector potential in the surface region. These authors found that the complete matrix element of $\vec{A}\cdot\vec{p}$ must be evaluated in that case. We shall show that a consistent model of photoemission from semi-infinite metals above the plasmon excitation energy must also account for the inherent spatial decay of the amplitude of the electromagnetic *far field* in the bulk.

The effects of the several different kinds of spatial variation of the vector potential on the photoemission from a free-electron metal have been discussed in the literature.[4,8-13] We shall analyze in some detail the effects of the spatial variation of the bulk or propagating far field, which, in a free-electron metal can be represented by a single transverse inhomogeneous plane wave. These effects have received relatively little attention compared to the much more extensive discussion of the effects of the spatial variation of the surface-bound near field, which inherently exhibits a longitudinal component.

Makinson,[4] Schiff and Thomas,[8] Endriz,[9] Feibelman,[10] Kliewer,[11] and most recently Maniv and Metiu[12] were all concerned with the spatial variation of the vector potential and/or its divergence in the surface region. Both effects are manifestations of the near field established by the incident photon flux at the surface. The amplitude of this near field, which in principle should be calculated self-consistently so as to include the dynamical response of the free electrons, typically decays quite rapidly with distance from the surface.[10-17] For photon energies below the bulk-plasmon excitation energy this near field represents the entire field. Recently, some authors attributed the surface photoeffect to the near field.[10,11,16] This presumably plausible rejection of the conventional interpretation of the surface photoeffect in terms of the gradient of the surface barrier raises the following questions:

(1) Does there exist a surface photoeffect which can be experimentally and unambiguously distinguished from the bulk effect, or is the distinction between surface and bulk effects model dependent?

(2) Is the surface photoeffect unique, or are there several contributions to this effect which are distinct and which correspond to different physical mechanisms?

For photon energies above the plasma excitation energy our analysis leads to a meaningful and model-independent identification of the bulk contribution to the "elastic" photoemitted current; that is, the contribution to the current due to strictly one-electron excitations as opposed to more complex excitations in which the photon energy is not entirely transferred to the single electron which is emitted. The remainder of the elastic current may, in general, be attributed to several distinct surface effects. Our analysis reveals a contribution to the current which is proportional to the classical free-electron result of Mitchell.[2] This contribution is also independent of the details of the near field at the surface. Other surface effects which are associated with this near field have been considered by Feibelman[10] and Kliewer.[11] Feibelman calculated the vector potential for the semi-infinite jellium self-consistently. His analysis was not devised to discriminate between the several factors contributing to the photoemitted current, though it evidently includes both a rapidly varying $\vec{A}$ and a longitudinal component of $\vec{A}$. Kliewer,[11] in a quasiclassical analysis, first identified the surface photoeffect as being exclusively due to the presence of a longitudinal component of the vector potential inside the solid.[11a] In a later publication Kliewer emphasized also the importance of the rapid spatial variation of the vector potential in the surface region.[11b] Mukhopadhyay and Lundqvist[17] (ML) discussed the physical mechanism responsible for the contribution of the longitudinal fields to the surface photoeffect. Above the bulk plasma frequency they identified it with the spontaneous decay of plasmon excitations into particle-hole excitations. Recently, Levinson and Plummer[16] reported the observation of a surface-related, enhanced photoemission from aluminum with the

use of p-polarized photons. They attributed this enhancement to the strong spatial variation of the vector potential in the surface region, a few angstroms wide. They emphasized that they did not observe contributions to surface photoexcitation by induced longitudinal fields, i.e., optically excited plasmons.

The spatial variation of the far field has been considered by Kliewer and Bennemann[13] in their analysis of bulk photoemission from a Drude model of a free-electron metal. In their analysis, Kliewer and Bennemann apply the photoabsorption probability calculated by Dumke[18] for an infinitely extended homogeneous metal and a spatially constant vector potential. In contrast, we treat explicitly the semi-infinite aspects of the problem. That is, we account for the effect of the surface both on the electronic states bound by a finite surface barrier, as opposed to the specularly reflecting (and impenetrable) barrier[11,13] of Kliewer and Bennemann (KB) and on the electromagnetic far fields which are subject to "outgoing-wave" boundary conditions rather than the symmetry imposed on them by KB. Recently, Maniv and Metiu[12] (MM) have achieved considerable progress in the calculation of the electromagnetic fields in the metal-vacuum interfacial region. These authors, who are primarily concerned with the near fields in the immediate vicinity of the interface, developed a scheme for a more general solution of Feibelman's[10] model. They were thus able to determine a dielectric response function which, in contrast to more conventional models, is continuous across the interfacial region. Maniv and Metiu applied their model and the three-step model of photoemission[19] to calculate the photoyield from a thin metallic film.[15] From their analyses MM conclude that, outside an interfacial region a few angstroms wide, their electromagnetic fields tend rapidly to the far fields obtained from the more conventional boundary matching solution of Maxwell's equations. This rather intuitive conclusion provides a more formal justification of the latter approach, as developed by Melnyk and Harrison[14] and others, in analyses of long-range surface effects manifest in the far fields.

Unlike Kliewer and MM, we do not use the three-step model. Instead, we apply the more fundamental scattering formalism introduced by Adawi.[5] We calculate the "matrix elements" for photoemission in terms of the explicitly spatially varying vector potential. Our improved treatment of the semi-infinite aspect of the system has led to several unexpected new results, and also a gratifying agreement with some intuitive expectations. The former unexpected results concern primarily the relation between "direct" and "nondirect" photoelectron transitions and the bulk and surface photoeffects. The latter more expected results concern several aspects of the "index-of-refraction corrections." Specifically, we found the following:

(1) In a semi-infinite system the direct, that is, wave-vector—conserving, transitions characterizing the translationally invariant infinite system persist, but are inherently associated with a continuous background of "directlike" transitions which conserve only the components of the wave vector parallel to the surface. For a free-electron metal the direct transitions are forbidden, just as for the strictly free electrons. However, the directlike transitions, which we shall show to represent a bulk effect, make an important contribution to the photoemitted current.

(2) There is a significant contribution to the photocurrent which involves neither direct nor directlike bulk transitions. This current is shown to correspond to the classical surface photoeffect first analyzed by Mitchell,[2] though enhanced by what may be interpreted as an interference with the bulk effect.[20] This contribution to the surface photoeffect is independent of, and unrelated to, any photoemitted current arising from the near-field region, that is, the region in which the vector potential may exhibit a significant spatial variation[10] and/or a longitudinal component which decays rapidly with distance from the surface.[11,17]

(3) The failure to conserve the component of the wave vector normal to the surface is not a unique feature of the surface photoeffect.

(4) Photoemission from a free-electron metal can occur only if the incident photon is p polarized. However, since the free-electron metal also exhibits a bulk photoeffect, this polarization (or "vectorial") effect can only serve to identify a free-electron-like contribution to the total photoemitted current, and not the surface effect as such.

(5) For p-polarized photons the photoemitted current is proportional to the squared magnitude of the amplitude of the electromagnetic field transmitted into the solid and inversely proportional to the magnitude of the transverse dielectric response function.

(6) For p-polarized photons the photoemitted current is a strong function of the photon angle of incidence and peaks sharply at the critical angle for total reflection.

(7) The high-photon-energy limit of the photoemitted energy distribution from a free-electron metal agrees with the corresponding limit for the atomic photoeffect. This is in contrast with the classical analysis of photoemission from a free-electron metal.[2]

The present analysis of photoemission from a free-electron metal provides the basis for a new and

more complete treatment of photoemission from a semi-infinite periodic solid. In particular, the directlike bulk contribution to the photoemitted current can be shown to be a general characteristic of photoemission from semi-infinite solids. That is, the wave-vector selection rule for bulk photoemission, derived in this paper for the FE model, can be extended to the semi-infinite three-dimensional periodic potential.[21]

The outline of the paper is as follows: The formal theory of photoemission from a FE model of a metal is developed in Sec. II. The Green-function formalism is reviewed in Sec. II A. This formalism is applied in Sec. II B to calculate the photoemitted current density for the classical free-electron model. Our more complete solution, which allows for a spatially varying vector potential is presented in Sec. II C. Here, the asymptotic dependence of the EDC on the photon energy and the vectorial effect are also discussed. A discussion and numerical analysis of the results is presented in Sec. III, and the conclusions are stated in Sec. IV.

II. THEORY OF PHOTOEMISSION FROM A FREE METAL

A. Green-function formalism

We shall calculate the photoelectric response in terms of a Green-function formalism to be described below. This technique allows photoemission to be viewed as an inelastic scattering process of the electrons; it has been discussed by others,[5-7] and so our remarks will be brief. While in the following we consider only single-electron excitations, the treatment can be extended to include other, more complex excitations, such as a single-electron excitation accompanied by a phonon or a plasmon emission (absorption).

The unperturbed system is described by the Hamiltonian $\mathscr{H}_0$ and its eigenstates $\{\Psi_0\}$,

$$\mathscr{H}_0\Psi_0(\vec{r},\vec{k})=E_0\Psi_0(\vec{r},\vec{k}) . \tag{1}$$

Here $\mathscr{H}_0$ includes both the electronic operator $\mathscr{H}_e$ and the free-field operator $\mathscr{H}_r$,

$$\mathscr{H}_0=\mathscr{H}_e+\mathscr{H}_r=-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})+\sum_\beta n_{\mathrm{op}}\hbar\omega_\beta ,$$

where $\mathscr{H}_r$ is written in second quantized notation, the sum on β is over all occupied states, and the constant zero-point energy term has been dropped in $\mathscr{H}_r$.

The radiation field induces a perturbation of $\mathscr{H}_0$ given by

$$\mathscr{H}'=\frac{ie\hbar}{mc}\vec{A}(\vec{r})\cdot\vec{\nabla}+\frac{1}{2}\frac{ie\hbar}{mc}\vec{\nabla}\cdot\vec{A}(\vec{r})+\frac{e^2}{2mc^2}A^2(\vec{r}) , \tag{2}$$

and consequently, the perturbed wave function satisfying "outgoing" boundary conditions can be written in the form

$$\Psi^{(+)}(\vec{r},\vec{k})=\Psi_0(\vec{r},\vec{k})+\Psi_s(\vec{r},\vec{k}) .$$

Here Ψ_0 represents the "incident" and Ψ_s the "scattered" component of $\Psi^{(+)}$. The complete wave function $\Psi^{(+)}(\vec{r},\vec{k})$ must be a solution of

$$[\mathscr{H}_0+\mathscr{H}'-(E+n_\beta\hbar\omega_\beta)]\Psi^{(+)}(\vec{r},\vec{k})=0 . \tag{3}$$

Noting that $\Psi^{(+)}$ may be expanded in a series of product states of the individual uncoupled electronic and radiation Hamiltonians, we approximate the unnormalized $\Psi^{(+)}$ by

$$\Psi^{(+)}\approx\Psi_0+\Psi_1=|n_\beta,\Phi_0\rangle+|(n_\beta-1),\Phi_1\rangle . \tag{4a}$$

Here Φ_0 is an eigenfunction of the unperturbed electronic problem for an energy E, namely

$$\mathscr{H}_e\Phi_0=E\Phi_0 . \tag{4b}$$

Φ_1 in Eq. (4a) is the perturbed electronic wave function having an energy $E+\hbar\omega$. It is determined by the requirement that Eqs. (3)—(4b) be consistent. Substituting Eqs. (4a) and (4b) into Eq. (3) we have

$$\mathscr{H}'|n_\beta,\Phi_0\rangle-(E+\hbar\omega-\mathscr{H}_e)|(n_\beta-1),\Phi_1\rangle+\mathscr{H}'|(n_\beta-1),\Phi_1\rangle=0 , \tag{4c}$$

where we hereafter replace $\hbar\omega_\beta$ by $\hbar\omega$.

Multiplying this equation from the left by $\langle n_\beta-1|$, and projecting out the corresponding component of the state of the radiation field, the following equation for Φ_1 is obtained:

$$\mathscr{H}'_{\mathrm{red}}\Phi_0-(E+\hbar\omega-\mathscr{H}_e)\Phi_1=0 , \tag{4d}$$

where in Eq. (4d) we denote by $\mathscr{H}'_{\mathrm{red}}$ the reduced operator,

$$\mathscr{H}'_{\mathrm{red}}=\langle n_\beta-1|\mathscr{H}'|n_\beta\rangle .$$

Henceforth we shall simplify our notation and drop the subscript from the symbol for the reduced operator; thus the operator $\mathscr{H}'$ acts only on the electronic eigenstates and is a c number with respect to the photon field. In deriving Eq. (4d) we also dropped the higher-order contributions $O(A^2)$.

The solution to Eq. (4d) for Φ_1 is

$$\Phi_1(\vec{r};\vec{k},E+\hbar\omega) = \int G_0(\vec{r},\vec{r}';E+\hbar\omega)\mathscr{H}'\Phi_0(\vec{r}';\vec{k},E)d\vec{r}' \ . \quad (5)$$

Here $G_0(\vec{r},\vec{r}';E')$ is the Green function of the unperturbed electronic system for the energy $E'=E+\hbar\omega$. In the present separable model G_0 may be determined by the Wronskian construction, to be discussed below.

In order to calculate the photoemitted current, it is convenient to introduce the correlation function $G^+(\vec{r},\vec{r}';E')$, which for zero temperature is[22] as follows:

$$G^+(\vec{r},\vec{r}';E')=i\Psi^{(+)*}(\vec{r}';\vec{k},E')\Psi^{(+)}(\vec{r};\vec{k},E') \ . \quad (6)$$

In the presence of a vector potential, the current density $\vec{j}(\vec{r};\vec{k},E')$ can be expressed in terms of $G^+(\vec{r},\vec{r}';E')$:

$$\vec{j}(\vec{r};\vec{k},E')=\left[\frac{e\hbar}{2m}(\vec{\nabla}'-\vec{\nabla})+\frac{ie^2}{mc}\vec{A}(\vec{r})\right] \times G^+(\vec{r},\vec{r}';E')\big|_{\vec{r}=\vec{r}'} \ . \quad (7a)$$

In general, $G^+(\vec{r},\vec{r}';E')$ may be represented by a perturbation (power) series in the amplitude of the vector potential,

$$G^+(\vec{r},\vec{r}';E')=G^+_{(0)}(\vec{r},\vec{r}';E')+G^+_{(1)}(\vec{r},\vec{r}';E') +G^+_{(2)}(\vec{r},\vec{r}';E') \ ,$$

where the subscripts indicate corresponding powers of the vector potential; thus $G^+_{(1)}(\vec{r},\vec{r}';E')$ is linear in $\vec{A}(\vec{r})$. In calculating the photoemitted current we are concerned only with terms which involve even powers of $\vec{A}(\vec{r})$. To the lowest order we require terms quadratic in $\vec{A}(\vec{r})$ which are consequently linear in the number of photons. Of the several terms contributing to the quadratic response function, we need to consider only the term

$$\frac{e\hbar}{2m}(\vec{\nabla}'-\vec{\nabla})G^+_{(2)}(r,r';E')\Big|_{\vec{r}=\vec{r}'} = \vec{j}_{(2)} \ , \quad (7b)$$

where the perturbed Green function $G^+_{(2)}$ accounts only for the perturbation $(ie\hbar/mc)\vec{A}(\vec{r})\cdot\vec{\nabla}$ and does not have to include the effect of the other second-order term $(eA/c)^2$, which does not contribute to the dc photoemitted current.[7] Thus the right-hand side of Eq. (7a) reduces to the current carried by the perturbed wave function Φ_1.

B. Photoemitted current density in simple FE models

1. Introduction

In this section we apply the Green-function technique to calculate the photoemitted current from a semi-infinite FE model. (See Fig. 1.) The unperturbed electronic Hamiltonian for the problem is

$$\mathscr{H}_e=-\frac{\hbar^2\nabla^2}{2m}-V_0\Theta(-z) \ , \quad V_0>0 \quad (8)$$

where $\Theta(z)$ is the unit step function. Following Mitchell we assume the vector potential in the solid to be a plane wave of constant amplitude $\hat{\epsilon}_{p,t}a_0Te^{i\vec{Q}\cdot\vec{r}}$, and taking the long-wavelength limit (or electric dipole approximation) we approximate $\vec{A}(\vec{r})$ by the constant field $\hat{\epsilon}_{p,t}a_0T$. Thus we consider the perturbation

$$\mathscr{H}'=\frac{ie\hbar}{mc}Ta_0(\hat{\epsilon}_{p,t}\cdot\vec{\nabla}) \ , \quad (9)$$

where a_0 is the incident amplitude of the vector potential, $\hat{\epsilon}_{p,t}$ is the polarization vector of the transmitted field for p-polarized light, and a_0T is the amplitude of the field transmitted into the solid. This particular form for $\mathscr{H}'$ explicitly neglects the photon momentum as well as any spatial dependence of the vector potential. We emphasize that these assumptions were made in the original analysis of the FE model by Mitchell,[2] as well as in its subsequent refinements by others.[5–7]

The symmetry of the model implies that the component of the wave vector of the electron parallel to the surface is conserved. Therefore, $G_0(\vec{r},\vec{r}';E')$ may be written as a two-dimensional Fourier series in $(\vec{\rho}-\vec{\rho}')$,

$$G_0(\vec{r},\vec{r}';E')=\frac{1}{L^2}\sum_{\vec{K}_\rho} e^{i\vec{K}_\rho\cdot(\vec{\rho}-\vec{\rho}')}g(z,z';\tilde{E}') \ , \quad (10)$$

where $\vec{\rho}$ and $\vec{\rho}'$ are two-dimensional vectors in the plane parallel to the surface. The "normal" energy $\tilde{E}'$ is defined by $\tilde{E}'=E'-\hbar^2K_\rho^2/2m$. The Fourier components $g(z,z';\tilde{E}')$ in the above series are the Green functions for a corresponding one-dimensional problem. This problem is derived from the full three-dimensional Schrödinger equation by a

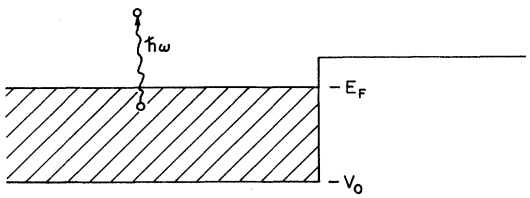

FIG. 1. Schematic representation of photoemission from a semi-infinite free-electron metal. The Fermi energy is denoted by $-(E_F+V_0)$, the depth of the square well is V_0, and the zero of energy is vacuum. The positive z axis is to the right.

separation of variables. Because $\mathscr{H}_e$ is a separable operator, the unperturbed eigenfunctions Φ_0 of $\mathscr{H}_e$ may be expressed in terms of the eigenfunctions of the "reduced" one-dimensional problem $\tilde{\mathscr{H}}_e$,

$$(\tilde{\mathscr{H}}_e-\tilde{E})\phi(z,\tilde{E})=\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}-V_o\Theta(-z)-\tilde{E}\right]\phi(z,\tilde{E})=0\ , \tag{11a}$$

$$\Phi_0(\vec{r},\vec{k},E)=\frac{1}{L^{3/2}}e^{i\vec{K}_\rho\cdot\vec{\rho}}\phi(z,\tilde{E})\ . \tag{11b}$$

In particular, the states bound in the semi-infinite square-well potential are given by

$$\phi(z,\tilde{E})=\begin{cases}\sqrt{2}\sin(\kappa_0 z-\delta)\ , & z<0\\ -\dfrac{\sqrt{2}\kappa_0 e^{-k_0 z}}{(\kappa_0^2+k_0^2)^{1/2}}\ , & z>0\end{cases} \tag{12a}$$

with

$$\kappa_0^2=\frac{2m}{\hbar^2}(\tilde{E}+V_0)\ ,\quad k_0^2=-\frac{2m}{\hbar^2}\tilde{E}>0\ ,$$

and

$$\sin\delta=\frac{\kappa_0}{(\kappa_0^2+k_0^2)^{1/2}}\ . \tag{12b}$$

On the other hand, the solutions for an energy $\tilde{E}'$ greater than zero are given by

$$\phi_1(z,\tilde{E}')=\begin{cases}e^{i\kappa z}+Ae^{-i\kappa z}\ , & z<0\\ (1+A)e^{ikz}\ , & z>0\end{cases} \tag{13a}$$

and

$$\phi_2(z,\tilde{E}')=\begin{cases}(1+B)e^{-i\kappa z}\ , & z<0\\ e^{-ikz}+Be^{ikz}\ , & z>0\end{cases} \tag{13b}$$

where

$$\kappa^2=\frac{2m}{\hbar^2}(\tilde{E}+V_0+\hbar\omega)\ ,\quad k^2=\frac{2m}{\hbar^2}(\tilde{E}+\hbar\omega)\ .$$

Continuity of the logarithmic derivative at the surface determines the coefficients A and B to be

$$A=-B=\frac{\kappa-k}{\kappa+k}\ . \tag{13c}$$

The perturbed wave function $\Phi_1(\vec{r},\tilde{E}')$ is obtained by substituting Eqs. (9), (10), and (11b) in Eq. (5). That is, retaining only the first-order term in the vector potential, we find

$$\Phi_1(\vec{r};\tilde{E}')=\frac{ie\hbar a_0 T}{mcL^{3/2}}(\hat{\epsilon}_{p,t}\cdot\hat{z})e^{i\vec{K}_\rho\cdot\vec{\rho}}\times\int_{-\infty}^{\infty}dz'g(z,z';\tilde{E}')\nabla_{z'}\phi(z',\tilde{E})\ , \tag{14}$$

where $\hat{z}$ is the unit vector in the z direction.

To evaluate the expression on the right-hand side of Eq. (14) it is necessary to calculate $g(z,z';\tilde{E}')$. This we shall do using the Wronskian construction[23] described below.

Denoting the two linearly independent eigenfunctions of the reduced Hamiltonian $\mathscr{H}_e$, which satisfy outgoing boundary conditions as z tends to $\pm\infty$, respectively, $\phi_1(z,\tilde{E}')$ and $\phi_2(z,\tilde{E}')$, we write

$$g(z,z';\tilde{E}')=-\frac{2m}{\hbar^2}\frac{\phi_1(z^>,\tilde{E}')\phi_2(z^<,\tilde{E}')}{W[\phi_1,\phi_2]}\ , \tag{15a}$$

with $z^>$ ($z^<$) being the greater (lesser) of z and z'. $W[\phi_1,\phi_2]$ is the Wronskian of these solutions and is given by

$$W[\phi_1,\phi_2]=\phi_1(z,\tilde{E}')\frac{\partial\phi_2(z,\tilde{E}')}{\partial z}-\frac{\partial\phi_1(z,\tilde{E}')}{\partial z}\phi_2(z,\tilde{E}')\ . \tag{15b}$$

Using Eqs. (13a) and (13b), we find the Wronskian to be

$$W[\phi_1,\phi_2]=-2ik(1+A)\ . \tag{15c}$$

In order to calculate the photoemitted current we require only the asymptotic value of Φ_1 as $z\to\infty$. Combining Eqs. (13) and (15) we obtain

$$g(z,z';\tilde{E}')=\frac{m}{i\hbar^2}\frac{e^{ikz}\phi_2(z')}{k}\ ,\quad z>0\ ,z'\ . \tag{15d}$$

Substituting the above into Eq. (14) we find, for $z\to\infty$,

$$\Phi_1(\vec{r};\vec{k})=\frac{ea_0}{\hbar c}\frac{T(\hat{\epsilon}_{p,t}\cdot\hat{z})}{kL^{3/2}}e^{i\vec{K}_\rho\cdot\vec{\rho}}e^{ikz}\times\int_{-\infty}^{\infty}\phi_2(z',\tilde{E}')\nabla_{z'}\phi(z',\tilde{E})dz'\ . \tag{16}$$

Here, the wave vector $\vec{k}$ has components parallel and perpendicular to the surface which are $\vec{K}_\rho$ and k, respectively. The integral on the right-hand side of Eq. (16) may be (and often is) interpreted as a "matrix element."[24] It is evaluated below.

2. Evaluation of the matrix element for the FE model

We now consider the problem of evaluating the integral in the last equation; thus, let

$$M \equiv \int_{-\infty}^{\infty} \phi_2(z';\tilde{E}')\frac{\partial}{\partial z'}\phi(z',\tilde{E})dz'$$
$$= \frac{i}{\hbar}\langle \phi_2^*(\tilde{E}') | p_z | \phi(\tilde{E}) \rangle . \quad (17)$$

The standard method of evaluating this integral which has been used in the past has been to invoke a certain matrix identity which will now be reviewed.[25] If $|i\rangle$ and $|f\rangle$ are eigenstates of $\mathscr{H}_e$ having eigenvalues ϵ_i and ϵ_f, respectively, then the matrix element M_{fi} satisfies the identity

$$M_{fi} = \frac{i}{\hbar}\langle f | \hat{\epsilon}_{p,t}\cdot\vec{p} | i \rangle = \frac{-\hat{\epsilon}_{p,t}}{\epsilon_f - \epsilon_i}\langle f | \vec{\nabla}\mathscr{H}_e | i \rangle . \quad (18)$$

The application of this result to photoemission has been discussed by Feibelman.[25] For the problem at hand,

$$\frac{\partial \mathscr{H}_e}{\partial z} = V_0\delta(z) ,$$

and the quantity M_{fi} defined by Eq. (17) reduces to

$$M_{fi} = -\frac{V_0}{\hbar\omega}\phi_2(z=0,\tilde{E}')\phi(z=0,\tilde{E}) . \quad (17')$$

Equation (17') explicitly indicates that in the present model, photoemission is strictly a surface effect, or rather a surface-sensitive effect. This result depends essentially on the applicability of the transformation of the matrix element indicated by Eq. (18), i.e., on the validity of the electric dipole approximation.

Using Eq. (12) for $\phi(z=0,\tilde{E}')$ in Eq. (16), we obtain the scattered component of the wave function,

$$\Phi_1(r,\tilde{E}') = \frac{2\sqrt{2}e(\hat{\epsilon}_{p,t}\cdot\hat{z})a_0 T}{\hbar c(\kappa+k)L^{3/2}}\frac{V_0}{\hbar\omega}\frac{\kappa_0}{(\kappa_0^2+k_0^2)^{1/2}} \times e^{i\vec{K}_\rho\cdot\vec{\rho}}e^{ikz} . \quad (19)$$

As noted in Sec. II A, the lowest-order contribution to the photoemitted current density is just the current density carried by $\Phi_1(r,\tilde{E}')$,

$$\vec{j}_{FE}(\vec{r};\vec{k}) = \frac{8eh}{mL^3}\left[\frac{ea_0}{\hbar c}\right]^2\left[\frac{V_0}{\hbar\omega}\right]^2\frac{|T|^2}{|\epsilon_T|}\frac{(\hat{\epsilon}_{p,i}\cdot\hat{z})^2}{(\kappa+k)^2} \times \frac{\kappa_0^2 k}{(\kappa_0^2+k_0^2)}\left[\hat{z}+\frac{\vec{K}_\rho}{k}\right] , \quad (20)$$

where carets denote unit vectors, and we have used Snell's law to express the z component of the polarization vector of the transmitted field, $\hat{\epsilon}_{p,t}\cdot\hat{z}$, in terms of the polarization vector for the incident p-polarized field, $\hat{\epsilon}_{p,i}$.

The total current density $\vec{J}(\vec{r})$ is obtained by including a factor of 2 to account for summation over spin, and integrating over the wave vectors of those initial states which contribute to the photoemission. The contribution to $\vec{J}(\vec{r})$ from the terms proportional to the vectors $\vec{K}_\rho$ cancels due to symmetry so that

$$\vec{J}(\vec{r}) = J(\vec{r})\hat{z} . \quad (21a)$$

Expressing κ, k, and k_0 in terms of κ_0, we find

$$J(\vec{r}) = \frac{2e\hbar}{m\pi^2}\left[\frac{ea_0}{\hbar c}\right]^2\left[\frac{V_0}{\hbar\omega}\right]^2\frac{(\hat{\epsilon}_{p,i}\cdot\hat{z})^2}{v_0}\frac{|T|^2}{|\epsilon_T|}\int_\alpha^{k_f}\frac{(k_F^2-\kappa_0^2)\kappa_0^2(\kappa_0^2+w-v_0)^{1/2}}{[(\kappa_0^2+w-v_0)^{1/2}+(\kappa_0^2+w)^{1/2}]^2}d\kappa_0 , \quad (21b)$$

where the several energies have been expressed in terms of quantities with the dimension of wave vector squared,

$$w = \frac{2m}{\hbar^2}\hbar\omega ,$$
$$v_0 = \frac{2m}{\hbar^2}V_0 , \quad (21c)$$
$$k_F^2 = \frac{2m}{\hbar^2}E_F ,$$

where E_F is the Fermi energy, and the lower limit of the integral in Eq. (21b) is defined by

$$\alpha = \max[0,(v_0-w)] . \quad (21d)$$

In Appendix A we evaluate analytically the integral in Eq. (21). For $\hbar\omega > V_0$ the exact result is

$$J(\vec{r})=\frac{2e\hbar}{m\pi^2}\left[\frac{ea_0}{\hbar c}\right]^2\frac{(\hat{\epsilon}_{p,i}\cdot\hat{z})^2}{v_0^3}\frac{|T|^2}{|\epsilon_T|}\left[\frac{V_0}{\hbar\omega}\right]^2$$
$$\times\left[\frac{k_F^3}{24}(k_F^2+w)^{3/2}(3w-8v_0-2k_F^2)\right.$$
$$-\tfrac{1}{8}\left[2k_F^2(w-v_0)+\frac{w}{8}(3w-8v-8k_F^2)\right]\{k_F(2k_F^2+w)(k_F^2+w)^{1/2}-w^2\ln[k_F+(k_F^2+w)^{1/2}]\}$$
$$+\frac{k_F^3}{24}(k_F^2+w-v_0)^{3/2}(2k_F^2-3w-v_0)+\tfrac{1}{8}[k_F^2(2w-v_0)-\tfrac{1}{8}(w-v_0)(8k_F^2-3w-v_0)]$$
$$\times\{k_f(2k_F^2+w-v_0)(k_F^2+w-v_0)^{1/2}$$
$$-(w-v_0)^2\ln[k_F+(k_F^2+w-v_0)^{1/2}]\}$$
$$-\frac{w^2}{8}\left[2k_F^2(w-v_0)+\frac{w}{8}(3w-8v_0-8k_F^2)\right]\ln(\sqrt{w})$$
$$\left.+\tfrac{1}{8}(w-v_0)^2[k_F^2(2w-v_0)-\tfrac{1}{8}(w-v_0)(8k_F^2-3w-v_0)]\ln(w-v_0)^{1/2}\right]. \tag{21e}$$

This result, although exact, is not particularly enlightening; it will be examined numerically in the next section. It is interesting to note, however, that upon differentiating $|\epsilon_T|J(\vec{r})|T|^{-2}$ with respect to the photon energy we find that this expression has a peak at $\hbar\omega=V_0$.[26] The quantity $|\epsilon_T||T|^{-2}J(\vec{r})$ corresponds to the yield in the absence of refraction effects and its peak at $\hbar\omega=V_0$ contradicts previous numerical results.[2] This point will be discussed further in Sec. III.

C. The photoemitted current density for FE Model in the presence of a spatially varying vector potential

1. Introduction: The far field

In this section we introduce a reformulation of photoemission from the FE model. This new theory imposes the important physical constraint that the photon flux must vanish at an infinite distance into the solid, that is,

$$\lim_{z\to-\infty}\vec{A}(\vec{r})=0\,.$$

We shall derive from this constraint the wave-vector selection rule for bulk photoemission from a semi-infinite free-electron metal. The analysis suggests a similar selection rule for photoemission from a semi-infinite periodic potential.[21] The expression for the photoemitted current suggests a reinterpretation of bulk and surface photoemission.

The matrix element M defined by Eq. (17) diverges. This mathematical difficulty represents the inconsistency of the classical FE model as a description of a thick metal with negligible photoabsorption. It is well known that in dealing with infinite systems mathematical difficulties may appear as a manifestation of an improper idealization of the physical system. An example is the well-known problem of calculating the Madelung potential in ionic crystals, which is represented by a conditionally convergent series.

In the present case one usually makes two idealizations:

(i) A large system is described by a semi-infinite model.

(ii) The near transparency of the solid is approximated by a vanishing optical absorption. Consequently, the vector potential far from the surface is represented by a transverse inhomogenous plane wave.

These two idealizations are not compatible: The physics of negligible absorption per unit length cannot be represented by the *zero*-absorption limit in a system of infinite extent unless the absorption is allowed to vanish *after* the calculation, whenever the dimensions of the system are much larger than the inverse attenuation length $1/\epsilon$. This dependence on the order of (nonuniform) limits is in no way peculiar; the adiabatic switching on of the interaction in the theory of interacting many-body systems exhibits the same kind of sensitivity. The physically motivated order of taking the limits of infinite

thickness and zero bulk absorptivity assures that the physically irrelevant region infinitely far from the surface, and the precise boundary conditions at infinity, do not unduly affect the calculated results. Specifically, for a finite value of ϵ only the region $|z| < z_M \sim 1/\epsilon$ contributes significantly to the integrals defining the matrix elements. The physical effects are characteristic of a region of width $1/\epsilon$.

Evidently in the limit $\epsilon \to 0$ this region includes the entire solid, provided that the limit is taken at the end of the calculation. Conversely, when ϵ is set equal to zero at the beginning, then the calculation in fact diverges, and a finite result can be extracted only by a convention such as followed in the conventional FE model. A physical interpretation of this mathematical procedure is that only strictly surface photoeffects are totally insensitive to the value of the bulk absorption, and exhibit a constant yield per unit area which is independent of the thickness of the photoemitter. In fact, the FE convention of evaluating the matrix element "eliminates" all bulk effects, i.e., both the strict bulk photoeffect and any possible bulk modification of "bare" surface effects. Thus, we conclude that a physically consistent model is obtained by allowing for a small, otherwise arbitrary optical-absorption constant and considering the limit of the photocurrent density as this absorption tends to zero. In this procedure, the vector potential in the solid is represented by an inhomogenous plane wave,

$$\vec{A}(\vec{r}) = \begin{cases} a_0 T \hat{\epsilon}_{p,t} e^{\epsilon z} e^{-i(\vec{Q}_\rho \cdot \vec{\rho} + q_T z)}, & z < 0 \\ a_0 (\hat{\epsilon}_{p,i} e^{-i(\vec{Q}_\rho \cdot \vec{\rho} + qz)} + R \hat{\epsilon}_{p,r} e^{-i(\vec{Q}_\rho \cdot \vec{\rho} - qz)}), & z > 0 . \end{cases} \tag{22}$$

Mathematically, the small optical-absorption coefficient ϵ is a convergence factor which will be set to zero at the end of the calculation. Inside the solid the components of the photon momentum $\vec{Q}_T$ parallel and perpendicular to the surface are denoted $\vec{Q}_\rho$ and q_T, respectively. Similarly, in vacuum, the incident-photon wave vector is denoted $\vec{Q} = (\vec{Q}_\rho, q)$. The photon-polarization vectors for the transverse, incident, and reflected fields are, respectively, denoted $\hat{\epsilon}_{p,t}$, $\hat{\epsilon}_{p,i}$, and $\hat{\epsilon}_{p,r}$. In Eq. (22), $a_0 R$ and $a_0 T$ are, respectively, the amplitudes of the reflected and transmitted vector potential. These may be determined from the classical Fresnel equation presented below. As shown by Melnyk and Harrison,[14]

$$R = \frac{\alpha - \beta}{\alpha + \beta}, \quad T = \frac{2\epsilon_T^{1/2} \cos\theta}{\alpha + \beta}, \tag{23}$$

where

$$\alpha = \epsilon_T(Q_T, \hbar\omega) \cos\theta$$

and

$$\beta = (\epsilon_T \sin^2\theta)^{1/2} . \tag{24}$$

From the boundary condition on the electromagnetic fields we find that R and T are related by

$$(1+R) = \epsilon_T^{1/2} T . \tag{25}$$

In Eqs. (23)–(25), θ is the photon angle of incidence measured from the normal, and $\epsilon_T(Q_T, \hbar\omega)$ is the transverse dielectric function of the solid. This dielectric function, which is derived from a long-wavelength approximation to the Boltzmann equation, satisfies the dispersion relation

$$\left[\frac{c}{\omega}\right]^2 \vec{Q}_T \cdot \vec{Q}_T = \epsilon_T(Q_T, \omega), \quad \vec{Q}_T = (\vec{Q}_\rho, q_T) \tag{26}$$

as well as the relation,

$$\epsilon_T = 1 - \frac{3\omega_p^2}{2\omega(\omega + i\tau^{-1})a^2} \left[\frac{1+a^2}{a} \arctan(a) - 1\right], \tag{27}$$

with

$$a^2 = -\frac{\vec{Q}_T \cdot \vec{Q}_T v_F^2}{(\omega + i\tau^{-1})^2} . \tag{28}$$

The simultaneous solution of Eqs. (26)–(28) determines both ϵ_T and the magnitude Q_T of the wave vector $\vec{Q}_T$ of the transverse wave in the solid as a function of ω. The components of $\vec{Q}_T$ may then be determined in terms of the photon angle of incidence.

In Eqs. (27) and (28), v_F is the Fermi velocity, ω_p is the (bulk-) plasma frequency, and τ is the electron lifetime. Equation (27) corresponds to an explicit model of the free-electron metal which allows us to account for the dispersive properties of the medium. To be consistent with the limit $\epsilon \to 0$, we shall also take $\tau^{-1} = 0$.

For completeness, we also give the optical transmittance $\tilde{T}$, which is the fraction of incident energy transmitted into the solid,

$$\tilde{T} = \frac{4\,\mathrm{Re}(\alpha^* \beta)}{|\alpha + \beta|^2} . \tag{29}$$

At this point it may be helpful to review the conditions under which the "far field," i.e., the vector potential far inside the bulk of a FE metal, can be represented by an inhomogenous transverse plane wave.

It is well known that above the bulk-plasmon energy $\hbar\omega_p$, metals are essentially transparent to electromagnetic radiation incident below the critical angle for total reflection.[27-29] Furthermore, in the energy range for which plasmons are well-defined elementary excitations, an incident photon excites at the surface a longitudinal polarization wave which may propagate, essentially without attenuation, into the bulk. The dispersion relation of these plasmons is implicitly defined by the zeroes of the longitudinal dielectric response functions,[28]

$$\epsilon_L(Q_L;\omega_p)=0\ ,\quad \vec{Q}_L=(\vec{Q}_\rho\ ,q_L)\ . \tag{26'}$$

As the wavelength decreases, these plasmons become increasingly more unstable against decay into particle-hole (single-particle—type) excitations.[30] The plasmon ceases to be a well-defined elementary excitation above a critical energy, when its dispersion relation merges into the particle-hole—excitation continuum, that is, when

$$\frac{(\hbar Q_L)^2}{2m}-\frac{\hbar^2K_FQ_L}{m}\le\hbar\omega_p(Q_L)\le\frac{(\hbar Q_L)^2}{2m}+\frac{\hbar^2K_FQ_L}{m}\ .$$

Here $K_F=[(2m/\hbar^2)E_F]^{1/2}$ is the Fermi wave vector. Evidently, the critical energy is roughly given by[30]

$$\hbar\omega_c=\hbar\omega_p(Q_L)=\frac{(\hbar^2Q_L)^2}{2m}+\frac{\hbar^2K_FQ_L}{m}\lesssim 3E_F\ .$$

Thus, when the incident photon has an energy larger than about $3E_F$, the longitudinal polarization fields excited at the vacuum-metal interface are strictly "near fields." Using the Lindhard dielectric function,[31] Mukhopadhyay and Lundqvist showed that these near fields decay at least as the inverse square of the distance from the surface.[32] In fact, the treatment of the longitudinal dielectric response function in the long-wavelength limit by Melnyk and Harrison[14] leads to the prediction of an exponential decay of the longitudinal fields for energies above $\hbar\omega_c$. It remains to note that, as pointed out by ML, the region of rapid charge variation and consequently rapid variation of $\vec{A}$ is even more restricted to the surface than that in which the longitudinal fields are significant. Thus, for photon energies $\hbar\omega>3E_F$ and at distances larger than $(\mathrm{Im}q_L)^{-1}\sim 10^{-7}$ cm,[33] Eq. (22) adequately represents the far field propagating into the solid. However, it does not provide an adequate representation of $\vec{A}(\vec{r})$ in the surface region a few angstroms wide where the vector potential may exhibit a significant longitudinal component and a rapid spatial variation. The recent work of Maniv and Metiu[12,15] further confirms these conclusions by explicit calculations.

2. *The scattered component of the wave function*

In order to obtain the perturbed or scattered component of the wave function at the energy $E+\hbar\omega$, we substitute Eqs. (10), (11b), and (22) into Eq. (5), and obtain for $z>0$,

$$\Phi_1(\vec{r};\vec{k})=\frac{ie\hbar a_0}{mcL^{3/2}}e^{i(\vec{K}_\rho-\vec{Q}_\rho)\cdot\vec{\rho}}\left[\int_{-\infty}^{0}g(z,z';\tilde{E}')\hat{z}\cdot\vec{A}(z')\frac{\partial}{\partial z'}\phi(z',\tilde{E})dz'\right.$$
$$+\int_0^z g(z,z';\tilde{E}')\hat{z}\cdot\vec{A}(z')\frac{\partial}{\partial z'}\phi(z',\tilde{E})dz'$$
$$\left.+\int_z^\infty g(z,z';\tilde{E}')\hat{z}\cdot\vec{A}(z')\frac{\partial}{\partial z'}\phi(z',\tilde{E})dz'\right]\ , \tag{30}$$

where $\vec{A}(\vec{r})=e^{-i\vec{Q}_\rho\cdot\vec{\rho}}\vec{A}(z)$. We shall be interested in the asymptotic values of $\Phi_1(\vec{r};\vec{k})$ and of the current as $z\to\infty$. In this limit the third integral tends to zero; therefore, in the following it will be neglected. Here we also note that the translational invariance in the plane of the surface implies that Φ_1 must be independent of the transverse component, A_x and A_y of the vector potential. Only the normal (z) component of $\vec{A}$ can perturb the electronic state and contribute to the photoemitted current from a free-electron metal.

The evaluation of the above integrals is readily accomplished. The unperturbed Green function g is defined by Eqs. (15), and the unperturbed wave function $\phi(z',\tilde{E})$ is given by Eq. (12). Upon evaluating the integrals, we find

$$\Phi_1(\vec{r};\vec{k})=\frac{ea_0}{\hbar kcL^{3/2}}(\hat{\epsilon}_{p,i}\cdot\hat{z})e^{i(\vec{K}_\rho-\vec{Q}_\rho)\cdot\vec{\rho}}e^{ikz}$$
$$\times\left[\frac{2k\kappa_0 T}{\sqrt{\epsilon_T}(\kappa+k)}\left[\frac{e^{-i\delta}}{\epsilon+i(\kappa_0-q_T-\kappa)}+\frac{e^{i\delta}}{\epsilon-i(\kappa_0+\kappa+q_T)}\right]\right.$$
$$+\sqrt{2}k_0\sin\delta\left[\frac{k_0(R+B)+i(k-q)(B-R)}{k_0^2+(k-q)^2}\right.$$
$$\left.\left.+\frac{k_0(BR+1)+i(k+q)(BR-1)}{k_0^2+(k+q)^2}\right]\right],\quad z\gg 0\,. \tag{31}$$

The phase δ is defined by Eq. (12b) and B is defined by Eq. (13c). Note that q_T is purely real when the photon angle of incidence is below the critical angle, and the lifetime of the photoexcited electrons is infinite.

The several wave vectors in Eq. (31) are obvious generalizations of the quantities introduced in Eqs. (12) and (13),

$$\kappa_0^2=\frac{2m}{\hbar^2}(E+V_0)-K_\rho^2\,,$$
$$k_0^2=-\frac{2mE}{\hbar^2}+K_\rho^2\geq 0\,,$$
$$\kappa^2=\frac{2m}{\hbar^2}(E+V_0+\hbar\omega)-(\vec{K}_\rho-\vec{Q}_\rho)^2\,,$$
$$k^2=\frac{2m}{\hbar^2}(E+\hbar\omega)-(\vec{K}_\rho-\vec{Q}_\rho)^2\,.$$

3. *The photoemitted current density and derivation of the wave-vector selection rule for bulk photoemission*

The calculation of the current density in the state Φ_1 is analogous to the corresponding classical calculation for the FE model discussed in Sec. II B. The result is rather complicated and therefore we shall first present a qualitative discussion of its features.

It is evident from Eq. (31) that the current density can be grouped into two terms which differ in their properties in the right half of the complex κ_0 plane. The first term has a pole in the right half of the complex κ_0 plane above the real axis. The second term is analytic. Hence we shall write

$$\vec{j}(\vec{r};\vec{k})=\vec{j}_B(\vec{r};\vec{k})+\vec{j}_S(\vec{r};\vec{k})\,, \tag{32}$$

where the singular term is denoted

$$\vec{j}_B(\vec{r};\vec{k})=\frac{\vec{R}}{\kappa_0-q_T-\kappa-i\epsilon}\,, \tag{33}$$

and the residue $\vec{R}$ is a nonsingular function of the several wave vectors.

The current $\vec{J}(\vec{r})$ is again obtained by integrating the current densities with respect to the wave vector $\vec{k}$,

$$\vec{J}(\vec{r})=\sum_{\alpha=B,S}\vec{J}_\alpha(\vec{r})=\hat{z}\sum_{\alpha=B,S}J_\alpha(\vec{r})$$
$$=\hat{z}\sum_{\alpha=B,S}\int j_\alpha(\vec{r};\vec{k})d^3k\,. \tag{34}$$

With the use of the relation[34]

$$\lim_{\epsilon\to 0}\frac{1}{(k-k')\pm i\epsilon}=P\frac{1}{k-k'}\mp i\pi\delta(k-k')\,, \tag{35a}$$

Eq. (33) gives

$$J_B(\vec{r})=P\int\frac{R_z}{\kappa_0-q_T-\kappa}d\kappa_0$$
$$+\pi i\int R_z\delta(\kappa_0-q_T-\kappa)d\kappa_0\,. \tag{35b}$$

The Dirac δ function in the second integral assures conservation of the normal or z component of momentum in the electronic transition involved in the photoemission process. P denotes the Cauchy principal part of the integral.

Equation (35a) essentially represents the selection rule for the z component of the wave vector in photoemission from semi-infinite solids. It is to be noted that quite generally the contributions of integrals of a principal part and the associated δ function, as indicated in Eq. (35), for example, are of comparable magnitude.[35] However, the physics of the free-electron model, which precludes single-photon absorption by a (free) electron, forces the integral over the δ function to vanish identically. The corresponding calculation of photoabsorption in an infinitely extended solid does not lead to the principal-part integral and introduces a multiplicative factor of 2 for the integral over the δ function, which corresponds to the familiar wave-vector selection rule for infinite solids. The principal-part integral is characteristic of the semi-infinite as opposed to the infinite solid. It represents an effect due to the existence of a surface, but not necessarily localized within the surface region. However, logically both terms in Eq. (35) should be interpreted as

"bulk" effects because in the limit $\epsilon \to 0$ the entire solid and not just a finite region of width $L \sim 1/\epsilon$ contributes to both photoabsorption and photoemission processes described by these two terms. When the electronic collision time τ is finite, one no longer has a strictly real q_T, and hence the imaginary part of j_B is no longer a δ function. However, it is sharply peaked when $\mathrm{Re}(q_T)$ conforms to the conservation of the z component of the momentum, i.e., $\mathrm{Re}(q_T)=\kappa_0-\kappa$. Thus the discussion of directlike transitions in photoemission remains qualitatively valid and meaningful as long as the collision time is sufficiently long to discriminate the direct transitions from the background of nondirect transitions. The preceding discussion can be shown to apply equally to photoemission from a three-dimensional semi-infinite periodic solid, subject to the usual replacement of wave vectors by the equivalent (modulo reciprocal-lattice vector) reduced wave vectors.[21]

When optical-refraction effects are neglected, that is, when one follows the conventional FE model in assuming $\epsilon_T \sim 1$, then $j_S(\vec{r};\vec{k})$ can be shown to reduce to an expression proportional to the conventional FE result. Therefore, it may be taken to represent a surface contribution to the photoemitted current. In order to facilitate the comparison between the current carried by the wave function specified by Eq. (31) and the current density derived earlier, we shall neglect the photon wave vector $\vec{Q}$ compared to the electronic wave vector.

A straightforward though tedious calculation gives

$$j_z(\vec{r};\vec{k})=[j_S(\vec{r};\vec{k})+j_B(\vec{r};\vec{k})] , \tag{36}$$

where

$$\begin{aligned} j_S(\vec{r};\vec{k})=j_0\{&v_0(2\kappa_0^2+w)+2|\epsilon_T|^2(v_0-\kappa_0^2)(v_0+w)-2\,\mathrm{Re}(\epsilon_T)w(v_0-\kappa_0^2) \\ &-2\,\mathrm{Im}(\epsilon_T)(v_0-\kappa_0^2)^{1/2}[\kappa_0-(\kappa_0^2+w)^{1/2}][v_0-\kappa_0^2-\kappa_0(\kappa_0^2+w)^{1/2}]\} , \end{aligned} \tag{37a}$$

$$j_B(\vec{r};\vec{k})=j_0\{w(\kappa_0^2-v_0)+2\,\mathrm{Re}(\epsilon_T)(v_0-\kappa_0^2)^{1/2}[v_0(\kappa_0^2+w)^{1/2}+\kappa_0(v_0+w)]+2\,\mathrm{Im}(\epsilon_T)w(v_0-\kappa_0^2)\} , \tag{37b}$$

and

$$j_0=\frac{e\hbar}{mL^3}\left[\frac{ea_0}{\hbar c}\right]^2\frac{8(\hat{\epsilon}_{p,i}\cdot\hat{z})^2}{(\hbar\omega)^2}\frac{|T|^2\kappa_0^2(\kappa_0^2+w-v_0)^{1/2}}{|\epsilon_T|v_0[(\kappa_0^2+w)^{1/2}+(\kappa_0^2+w-v_0)^{1/2}]^2} , \tag{37c}$$

where $\mathrm{Re}(\epsilon_T)$ and $\mathrm{Im}(\epsilon_T)$ denote, respectively, the real and imaginary parts of the transverse dielectric constant evaluated for the wave vector $\vec{Q}_T(\omega)$ and the frequency ω.

It should be emphasized that this result is obtained only if the limit $\epsilon \to 0$ is taken at the end of the calculation. On the other hand, if this limit is taken at the beginning of the calculation then, as discussed above, one obtains the conventional current density for the FE model, j_{FE}, presented in Eq. (20). In obtaining Eqs. (36) and (37) we have used Eq. (25) to express the current density in terms of $|T|^2$.

We already discussed the reason for identifying $j_B(\vec{r};\vec{k})$ with the bulk contribution to the photoeffect. This contribution, specified by Eq. (35), consists of two terms: One is proportional to a δ function which assures conservation of the component of the momentum normal to the surface. In an infinite translationally invariant system this term is multiplied by a factor of 2. The corresponding electronic bulk transitions are called direct.

The second term is the principal part which is *always* associated with the particular representation of the δ function presented in Eq. (35a). This term represents the effect of bulk transitions which do not conserve the component of the momentum or rather (reduced) wave vector normal to the surface, although they conserve the components of the wave vector parallel to the surface. We shall refer to these latter transitions as directlike.[36]

The remaining contribution to the EDC, denoted by j_S, is to be identified as an enhanced surface photoeffect. The term "enhanced" is to stress that the current is not necessarily exclusively due to emission from the surface region. It may include a contribution from the interference of bulk and surface components of the electronic wave functions. This point is clearly indicated by the simultaneous limit of a long photon wavelength and high photon energy ($Q \to 0, \omega \to \infty$). In the long-wavelength limit,

$$\epsilon_T=1-\left[\frac{\omega_p}{\omega}\right]^2 . \tag{38}$$

Thus in the high-energy limit, $\epsilon_T \sim 1$, and we obtain from Eqs. (20), (36), and (37),

$$\left[2+\frac{\hbar\omega}{V_0}\right]j_{\mathrm{FE},z}(\vec{r};\vec{k})=j_S(\vec{r};\vec{k}) . \tag{39}$$

We note that if the matrix element for photoemission is transformed into a gradient of the potential, as indicated by Eq. (18), then one obtains $j_{\mathrm{FE},z}$, and not j_S. Stated differently, if this transformation is performed then one loses the bulk contribution and with it the enhancement factor, i.e.,

$$2+\frac{\hbar\omega}{V_0}\rightarrow 1 .$$

That is, the classical or bare surface effect discussed by Mitchell[2] and others[5–7] is recovered.

4. *Asymptotic dependence of PEED on the photon energy*

In the conventional normalization of the photoemitted energy distribution (PEED) one divides the current density by the incident photon flux F where

$$F=\frac{\omega^2 |a_0|^2\cos\theta}{2\pi c(\hbar\omega)} . \tag{40}$$

It is remarkable that the asymptotic photon-energy dependence of our expression for the PEED is

$$j/F\sim O(\hbar\omega)^{-5/2} . \tag{41}$$

This is in sharp contrast to the corresponding expression obtained from the conventional treatment of photoemission from an FE model,

$$j_{\mathrm{FE}}/F\sim O(\hbar\omega)^{-7/2} . \tag{42}$$

Equation (41), in contrast to Eq. (42), agrees with the asymptotic photon-energy dependence of the transition rate for the atomic photoeffect.[37] This result is expected on physical grounds: As the photon energy tends to infinity, the difference between the atomic and square-well potentials should become unimportant. Thus, it is reasonable to impose on any model of photoemission the requirement that it satisfy Eq. (41).

5. *Polarization dependence of the PEED*

We shall now examine the polarization dependence of the PEED which is given by Eq. (37). We assume the light to be incident at an angle θ from the normal to the solid. Substituting Eq. (40) for the photon flux into Eq. (37), we have

$$\frac{j_z(\vec{r},\vec{k})}{F}=\frac{2\pi ce}{\omega mL^3}\left[\frac{e}{c}\right]^2\frac{\sin^2\theta}{\cos\theta} \times[j'_B(\vec{r},\vec{k})+j'_S(\vec{r},\vec{k})] , \tag{43}$$

where we displayed explicitly the angular dependence of the photoemitted current, by writing

$$j_{B,S}=\frac{e\hbar}{mL^3}\left[\frac{ea_0}{\hbar c}\right]^2\sin^2\theta j'_{B,S} .$$

In the preceding we have assumed the photon to be polarized in the plane of incidence (p polarization). The angular dependence exhibited in Eq. (43) is the same as that found by Mitchell[2] and others.[4] The role of the photon polarization and its consequences, i.e., the vectorial effect, are well known and have been used to separate the bulk and surface effects in conventional analyses of photoemission.[38] The separation is based on the identification of a contribution to the photoemitted current which depends only on A_z, and hence is characteristic of p-polarized photons. This polarization dependence has been previously identified as characteristic of, and peculiar to, the surface photoeffect. This identification is apparently motivated by the classical analysis of the FE model which, as discussed in Sec. I, determined only the surface photoeffect. The analysis of the FE model in Sec. II C 3 indicates the presence of a bulk contribution to the photoemitted current which also depends only on the component of the vector potential normal to the surface. For models with a separable potential, and only for those, the entire photocurrent depends only on A_z. Therefore we conclude that the vectorial effect allows only the identification of a free-electron-like contribution to the photoemitted current. This free-electron-like contribution includes both surface and bulk contributions, and is characteristic of any separable or effective mass type model of the semi-infinite solid.

6. *Dependence of PEED on the angle of incidence and critical angle of incidence*

The effect of the angle of incidence of the photon is illustrated in Fig. 2 for a model metal with surface barrier height $V_0=10$ eV, Fermi energy $E_F=5$ eV, and plasma energy $\hbar\omega_p=8.36$ eV. The photoyield, given by the solid curve, is calculated by an integration of Eq. (36) over the initial wave vector of the electron, including a factor of 2 for spin. It is to be noted that the photoyield has a sharp peak at the critical angle θ_c for total reflection from the vacuum-metal interface. This angle is specified by the relation

$$\mathrm{Re}(\epsilon_T)-\sin^2\theta_c=0 . \tag{44}$$

Physically, the peak in the photoyield arises from the proportionality of the photoyield to the intensity of the transmitted electromagnetic field inside the solid. More precisely, the EDC depends on the

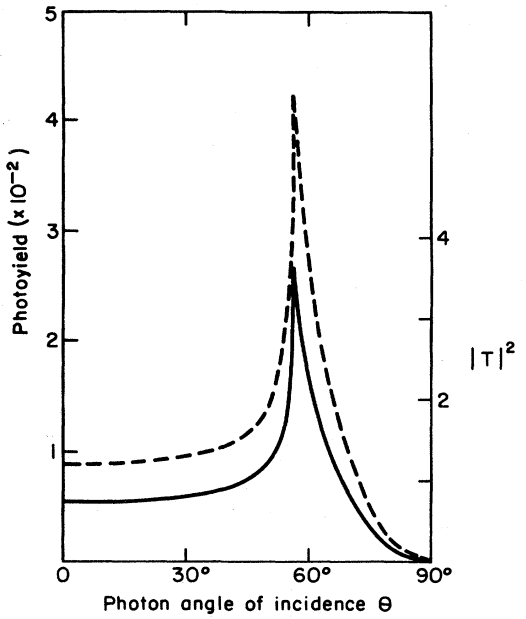

FIG. 2. Photoyield (in units of electrons/cm^2 of emitter per transmitted photon) and the intensity of the transmitted electromagnetic field $|T|^2$ vs the photon angle of incidence θ (dashed curve). The photon energy is 15 eV; in plotting the photoyield the factor $\sin^2\theta/\cos\theta$ has been omitted.

squared magnitude of the amplitude transmission coefficient $|T|^2$, which has a sharp cusp at the critical angle and decreases rapidly with the angle of incidence for $\theta > \theta_c$. In Fig. 2 this general behavior of $|T|^2$ is clearly illustrated.[39]

The presence of a peak in the photoyield (at fixed photon energy) as a function of the angle of incidence is well known and several possible explanations for its existence have been offered in the past.[40,41] More recently, Rowe, in studying the effect of Cl deposited on a Si(111) surface, has noted that the photoyield is strongly influenced by $|A_z|^2$ at the surface.[42] Furthermore, with increasing photon energies the peak shifts to larger angles of incidence. Both of these observations are consistent with the results presented here. In fact, the presence of a peak in the photoyield at the critical angle for total reflection has been noted previously[11(b)] and has been used to study the dielectric function of the photoemitter.[43]

It should be noted that for angles larger than the critical angle, the vector potential is an inhomogeneous plane wave,

$$\vec{A} = a_0 T \hat{\epsilon}_{p,t} \exp\{-i[(\vec{Q}_\rho \cdot \vec{\rho} + \mathrm{Re}(q_T)z] + \mathrm{Im}(q_T)z\}, \quad z<0$$

where $\mathrm{Im}(q_T)$ is an increasing function of θ. Thus with increasing $\theta > \theta_c$ the penetration of the electromagnetic field into the solid decreases and hence, in this sense, the photoelectric effect becomes increasingly surface sensitive.[44]

III. DISCUSSION AND NUMERICAL ANALYSIS

In the present section we complement the formal analysis of the photoemitted current density and PEED by an explicit numerical analysis of Eqs. (20), (36), and (37) for the typical model parameters specified in Sec. II C 6. In comparing our results with those of the conventional FE theory, it is convenient to distinguish two regimes of photon energy, namely $\hbar\omega \lesssim V_0$.

In Fig. 3 we compare, at a photon energy less than V_0 and an angle of incidence equal to 15°, the PEED's predicted by the simple FE model and our theory.[45] We also display the bulk contribution in our theory. The plots of the total PEED and of the bulk contribution to this energy distribution j_B are generally similar; the importance of $j_B(\vec{r};\vec{k})$ is evident. Specifically, for $\hbar\omega = 9$ eV the surface and

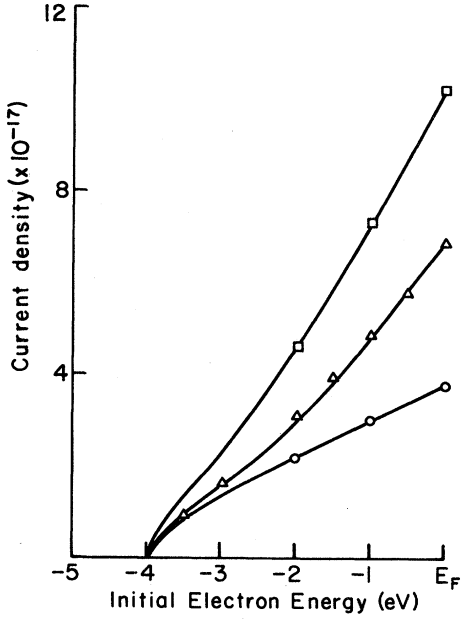

FIG. 3. Photoemitted current density (electrons/cm^2 of emitter per s) as a function of initial electron energy for a photon of energy $\hbar\omega = 9$ eV incident at 15°. The curves are labeled by squares (□) for our result [Eq. (36)], triangles (△) denote the bulk contribution to the current density [Eq. (37b)], while circles (○) denote the result for the conventional FE model [Eq. (20)].

bulk contributions to the PEED are approximately equal. For this particular photon energy the critical angle θ_c is approximately 22°.

In Fig. 4 we present the same quantities as in Fig. 3 but for $\hbar\omega > V_0$. Again we note that the contribution of $j_B(\vec{r};\vec{k})$ is significant. Figures 2—4 illustrate the following general trends:

(i) Both our calculated PEED, Eq. (36), and the bulk component of the PEED, Eq. (37b), are larger than the classical FE values.

(ii) For a fixed photon energy both the bulk and surface contributions to the calculated PEED increase as the initial electron energy approaches the Fermi energy. This may be interpreted as a consequence of the monotonic increase in the density of initial states with energy.

(iii) The bulk and surface contributions are approximately equal. This fact is further illustrated by the plots of the normalized bulk and surface contributions in Fig. 5.

(iv) The photoemitted current at a given initial energy decreases rapidly for larger photon energies. This trend is even more evident in the plot of total photocurrent versus photon energy, Fig. 6.

(v) For a fixed photon energy and variable angle of incidence the photoyield peaks at the critical angle for total reflection.

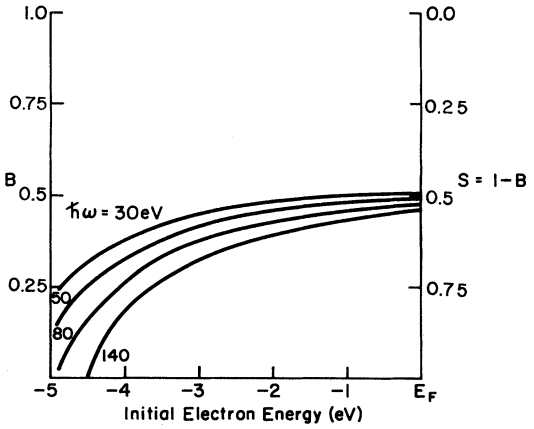

FIG. 5. Comparison of the bulk (B) and enhanced surface (S) contributions to photoemission defined by Eqs. (45) as a function of initial electron energy. The curves are labeled by the photon energy. The photon angle of incidence is 45° which is below the critical angle.

It is convenient to introduce the quantities B and S representing, respectively, the normalized bulk and

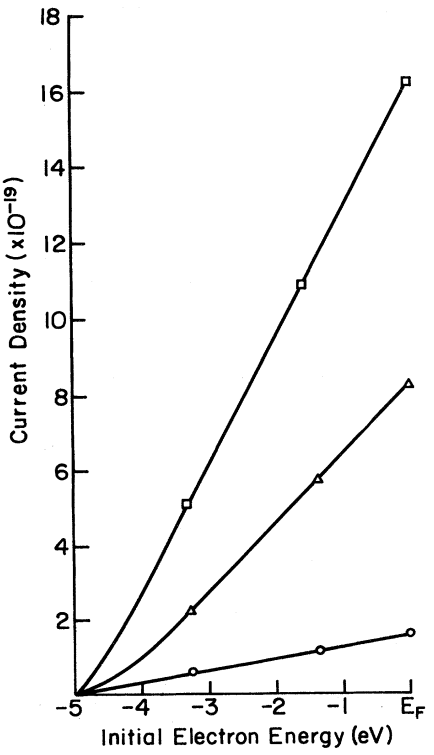

FIG. 4. Photoemitted current density (electrons/cm^2 of emitter per s) as a function of initial electron energy for a photon energy $\hbar\omega = 30$ eV incident at 15°. The notation is the same as that of Fig. 3.

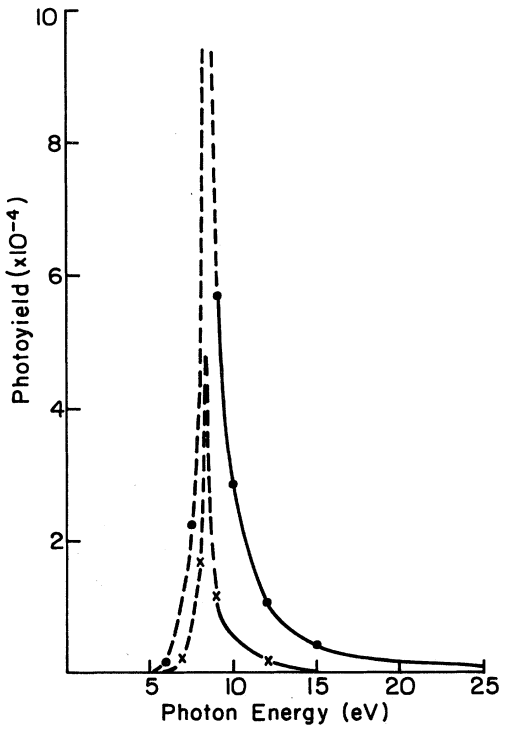

FIG. 6. The photoyield (electrons/cm^2 of emitter per transmitted photon) as a function of incident photon energy. Our results are denoted by ● and the classical result by ×. For both results the dashed curves indicate the region for which our theory is not applicable.

surface contributions to $j(\vec{r};\vec{k})$ and defined by

$$B=\frac{j_B(\vec{r};\vec{k})}{j_B(\vec{r};\vec{k})+j_S(\vec{r};\vec{k})} \tag{45a}$$

and

$$S=1-B\ . \tag{45b}$$

Plots of B and S for several photon energies are presented in Fig. 5. Here we note that as the photon energy increases, the bulk contribution to our calculated current density decreases particularly for small initial electron energies. Therefore, the "surface contribution" to the PEED seems to increase with increasing photon energy.

A plot of the photoyield versus photon energy for both our model and the FE model is shown in Fig. 6. The previously discussed difference in the asymptotic photon-energy dependence of the two current densities is evident. The yield appears to peak at $\hbar\omega=\hbar\omega_p$; however, our model applies only when $\hbar\omega>\hbar\omega_p$. For these large energies our model correctly predicts a monotonic decrease of the yield with energy and in particular, the asymptotic dependence of Y on $\hbar\omega$. On the other hand, the apparent peak at $\hbar\omega_p$ is due to the neglect of the near-field effects which in fact lead to a minimum at $\hbar\omega_p$.[16] The quantity $|\epsilon_T|\,|T|^{-2}J(\vec{r})$ peaks at $\hbar\omega=V_0$ and drops rather sharply beyond this point. This seems to be an unexpected result, since this quantity might be expected to saturate for $\hbar\omega\geq V_0$, i.e., when the photon energy is large enough for the most tightly bound electrons to be photoemitted. The physical reason for the maximum is the ultimately monotonic decrease in the scattering cross section as the photon energy increases indefinitely. Mathematically, this decrease in the scattering cross section is accounted for by the normalization of the Green function.[46]

IV. CONCLUSION

A new and consistent model was formulated for photoemission from a free-electron metal with vanishingly small optical absorption above the plasmon energy. The model which applies only above the plasma excitation energy eliminates the physical and mathematical difficulties inherent in the classical FE model of photoemission. This is achieved by representing the vector potential in the far-field region in terms of an attenuated (inhomogenous) plane wave and correctly taking the nonuniform limit of a vanishing attenuation for a semi-infinite system.

The selection rule for the wave vector in bulk photoemission from a semi-infinite solid was derived and associated with a new directlike contribution to the bulk photoeffect due to electronic transitions that conserve the components of momentum (wave vector) parallel to the surface, but do not conserve the component of momentum normal to the surface. This contribution was shown to be intimately connected to the conventional direct wave-vector—conserving (bulk) transitions, which are forbidden in FE metals. Both types of transitions contribute to the photoeffect when the periodic (bulk) potential is included in the model.[21] It is demonstrated that in the FE metal only directlike transitions represent strictly bulk contributions to the photoeffect. This then associates the remaining photoemitted current with one of several possible surface photoeffects. A bulk enhancement of the classical FE surface photoeffect was identified and discussed: We define surface contributions to the photoeffect to be those contributions that are explicitly insensitive to the bulk. These are in particular insensitive to the value ϵ of the optical-absorption constant in the *asymptotic far-field region.* Hence the bare surface photoeffect is obtained by taking the limit $\epsilon\rightarrow 0$ at the beginning of the calculation. This leads, for the free-electron metal, to the classical FE result $j_{\mathrm{FE},z}(\vec{r};\vec{k})$ presented in Eq. (20). The difference between this expression and our result $j_S(\vec{r};\vec{k})$ given by Eq. (37) evidently represents a bulk modification of the surface effect. This conclusion is corroborated by the high-photon-energy limit of j_S, given in Eq. (39), which can be rewritten as

$$j_S(\vec{r};\vec{k})=\left[1+\left[1+\frac{\hbar\omega}{V_0}\right]\right]j_{\mathrm{FE},z}(\vec{r};\vec{k})\ . \tag{39b}$$

The term $(1+\hbar\omega/V_0)j_{\mathrm{FE},z}$ is a measure of the sensitivity of j_S to the bulk, and hence it may be interpreted as a manifestation of the interaction between bulk and surface photoemission. In the FE model this interaction always leads to an increase of j_S. Here it is interesting to note the investigation by Schaich and Ashcroft[20] (SA) of photoemission from a one-dimensional model metal with a periodic potential: Using a definition of surface and bulk photoeffects which differs from the one proposed in the present work, SA find both constructive and destructive interference between the two photoeffects.

In Sec. I we raised two fundamental questions concerning the surface photoeffect which now can be answered at least in part: There clearly exists no unique surface photoeffect in the free-electron metal. Our discussion of a surface photoeffect in no way contradicts the several analyses of the spatial variation of the vector potential in the surface region[8–17] and the associated photoemitted current density. There are several distinct though related mechanisms of surface photoemission from FE metals associated, for example, with the rapid variation

of the vector potential in the surface region,[10,11(b),15,16] the decay of the longitudinal polarization fields (plasmons),[11(b),14,17] and the spatial variation of the (self-consistent) surface barrier.[4,10] The corresponding contributions to the photoemitted current may also be affected in varying degrees by the bulk. This was demonstrated by us for the case of the contribution associated with the spatial variation of the surface barrier.

It is characteristic of all surface photoeffects that the corresponding electronic transitions do not conserve the component of the wave vector normal to the surface. However, as we have shown, the direct-like bulk transitions also are of this type. Hence nonconservation of k_z is necessary but not sufficient to identify a strictly surface contribution to the photoemitted current.

In the past the vectorial effect has been assumed to allow an experimental separation of bulk and surface contributions to the photoemitted current. Our analysis of the polarization dependence of the photoemitted energy distribution indicates that the bulk contribution to the photoeffect in the FE metal has the same polarization dependence as the (enhanced) surface contribution. Thus the vectorial effect characterizes the FE contribution as a whole, rather than just the surface contribution, and hence cannot be used to discriminate between the bulk and surface contributions.

The preceding clearly does not preclude experimental configurations tending to increase the relative contribution of electron emission from the surface region. One common technique of reducing the effective penetration depth of the photons is to operate at nearly grazing incidence. The reduced penetration is a direct consequence of the approximately isotropic optical absorptivity. We have shown that a similar effect occurs for photons incident at angles larger than the critical angle $\theta_c(\omega)$ for total reflection. Here it is the imaginary part of q_T, the component of the photon wave vector in the metal which is normal to the surface, which leads to an exponential spatial decay of the vector potential. In this case, the exponential decay does not necessarily depend on any optical absorption. Photons incident at angles larger than $\theta_c(\omega)$ evidently present a more practical experimental configuration than photons at grazing incidence for increasing the surface sensitivity of photoemission.

A strong peak in the photoelectric yield at the critical angle of incidence was predicted. This is in agreement with previous observations,[42] and is expected to be of practical interest.

ACKNOWLEDGMENT

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APPENDIX: EXACT INTEGRATION OF MITCHELL'S CURRENT DENSITY

In this appendix the evaluation of the integral which appears in Eq. (21a) is given. We define

$$J_1 \equiv \int_a^{k_F} \frac{(k_F^2-\kappa_0^2)\kappa_0^2(\kappa_0^2+w-v_0)^{1/2}d\kappa_0}{[(\kappa_0^2+w-v_0)^{1/2}+(\kappa_0^2+w)^{1/2}]^2} . \tag{A1}$$

Rationalizing the denominator, we find

$$J_1=\frac{1}{v_0^2}\int((k_F^2-\kappa_0^2)\kappa_0^2(\kappa_0^2+w-v_0)^{1/2}\{2(\kappa_0^2+w)-v_0-2[(\kappa_0^2+w-v_0)(\kappa_0^2+w)]^{1/2}\})d\kappa_0 . \tag{A2}$$

Expanding this expression, we obtain

$$\begin{aligned} J_1=\frac{1}{v_0^2}\Bigg[& 2\int\kappa_0^6(\kappa_0^2+w)^{1/2}d\kappa_0+2(w-v_0-k_F^2)\int\kappa_0^4(\kappa_0^2+w)^{1/2}d\kappa_0 \\ & -2k_F^2(w-v_0)\int\kappa_0^2(\kappa_0^2+w)^{1/2}d\kappa_0-2\int\kappa_0^6(\kappa_0^2+w-v_0)^{1/2}d\kappa_0 \\ & -(2w-v_0-2k_F^2)\int\kappa_0^4(\kappa_0^2+w-v_0)^{1/2}d\kappa_0+(2w-v_0)k_F^2\int\kappa_0^2(\kappa_0^2+w-v_0)^{1/2}d\kappa_0\Bigg] . \end{aligned} \tag{A3}$$

All of the above integrals may be evaluated rather easily. Using Eq. (21c), we find that when the lower limit is zero the result is given by Eq. (21e). On the other hand, if $\hbar\omega < V_0$, we obtain the following:

$$
\begin{aligned}
J(\vec{r}) = & \frac{2e\hbar}{m\pi^2}\left[\frac{ea_0}{\hbar c}\right]^2 \frac{(\hat{\epsilon}_{p,i}\cdot\hat{z})}{v_0^3}\left[\frac{V_0}{\hbar\omega}\right]^2 \frac{|T|^2}{|\epsilon_T|} \\
& \times \left[\frac{k_F^3}{24}(k_F^2+w)^{3/2}(3w-8v_0-2k_F^2)-\frac{1}{8}\left[2k_F^2(w-v_0)+\frac{w}{8}(3w-8v_0-8k_F^2)\right]\right. \\
& \qquad \times\{k_F(2k_F^2+w)(k_F^2+w)^{1/2}-w^2\ln[k_F+(k_F^2+w)^{1/2}]\} \\
& +\frac{k_F^3}{24}(k_F^2+w-v_0)^{3/2}(2k_F^2-3w-v_0) \\
& +\frac{1}{8}\left[k_F^2(2w-v_0)-\frac{w-v_0}{8}(8k_F^2-3w-v_0\right]\{k_F(2k_F^2+w-v_0)(k_F^2+w-v_0)^{1/2} \\
& \qquad -(w-v_0)^2\ln[k_F+(k_F^2+w-v_0)^{1/2}]\} \\
& +\tfrac{1}{24}[v_0(v_0-w)]^{3/2}(2v_0-3w-8k_F^2) \\
& +\frac{1}{8}\left[2k_F^2(w-v_0)+\frac{w}{8}[3w-8(v_0+k_F^2)]\right]\{[v_0(v_0-w)]^{1/2}(2v_0-w)-w^2\ln(\sqrt{v_0}+\sqrt{v_0-w})\} \\
& \left.+\tfrac{1}{8}(w-v_0)\ln(v_0-w)^{1/2}\left[k_F^2(2w-v_0)-\frac{w-v_0}{8}(8k_F^2-3w-v_0)\right]\right] \qquad \text{(A4)}
\end{aligned}
$$

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[45]In calculating the current densities displayed in Figs. 3 and 4, it is necessary to have a value of a_0 [see Eq. (20), for example]. This was obtained by assuming an incident photon flux of 10^9 photons/s, from which a_0 may be calculated; see Eq. (40).

[46]The Green function is normalized in the sense that for $\hbar\omega\to\infty$, $g(z,z';\bar{E}')\to 0$. This follows directly from Eqs. (15a) and (15c) and the fact that $k\propto(\hbar\omega)^{1/2}$.