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Influence of Refraction of p-Polarized Light on Photoemission from Metallic Surface States

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The refraction of p-polarized light at a metal surface leads, under certain circumstances, to a large peak in the spatial distribution of the normal component of the electric field near the surface. The origin of this peak is explained both in terms of a classical correspondence and in terms of a theory based on the non-local dielectric response of the metal surface. The significance of the large magnitude and rapid variation of the surface electric field in exciting photoelectrons from surface states is discussed.

A refração de luz p-polarizada em uma superfície metálica leva, sob certas circunstâncias, a um grande pico na distribuição espacial da componente normal do campo elétrico perto da superfície. A origem desse pico é explicada tanto em termos de uma correspondência clássica quanto em termos de uma teoria baseada na resposta dielétrica não-local da superfície do metal. A relevância da grande magnitude e da rápida variação do campo elétrico na superfície na excitação de fotoelétrons de estados da superfície é discutida.

Photoemission from surface states of metals as a function of the frequency of light has generated considerable interest and controversy in recent times. In this paper we study the refraction of p-polarized light at a metal surface to see what influence refraction has on the process of photoexcitation. We conclude that the reflection and refraction of light can help us understand and interpret correctly certain intriguing aspects of the experimental photoemission data, especially those regarding the frequency dependence.

The basic difference between the reflection of s-polarized light and p-polarized light by a dielectric medium lies in the difference of boundary conditions at the reflecting surface. Whereas the components of the electric field parallel to the surface are continuous across the boundary, it is the component of the displacement field normal to the surface which must be continuous. If the dielectric medium can be represented adequately by a local and isotropic but spatially varying dialectric constant

$$\varepsilon_{\omega}(z)\; E^{z}_{\vec{Q},\omega}(z) = \text{constant}, \qquad \lambda \gg a, \tag{1}$$

where λ is the wavelength of light and a is a length characterizing the diffuseness of the surface, Here we have made use of the translational invariance of the problem in the xy-plane to Fourier-transformall fields in that plane and in time, so that

$$E^{\mu}(\vec{r},t) = E^{\mu}_{\vec{Q},\omega}(z)\; e^{i(\vec{Q}\cdot\vec{\rho} - \omega t)}\;, \tag{2}$$

where μ stands for any Cartesian component, $\vec{\rho} = \hat{x}x + \hat{y}y$, $Q = (\omega/c)\ \text{Sin}\ \theta_i = (2\pi/\lambda)\ \text{Sin}\ \theta_i$, and θ_i is the angle of incidence. Equation (1) shows the z-component of the electric field for p-polarized light will be singular if the local dielectric constant (assumed real) vanishes. This feature of light propagation in an inhomogeneois dielectric medium is well-known in classical electrodynamics[1]. It is also clear[1] that the presumed singularity of $E^{z}(z)$ will be rounded to a peak when one recognizes the fact that $\varepsilon_{w}(z)$ is in general complex and not real. Figure 1 snows the spatial variation of the normal component of the electric field near a metal surface in a idealized model caiculation where the metal occupies the half-space $z < 0$, and its dielectric response is assumed to be given by the function $\varepsilon_{w}(z) = 1 - 4\pi\, e^{2}\, n_{0}(z)/m\omega^{2}$, $n_{0}(z)$ being the local electron density. We consider a simple model where $n_{0}(z) = n_{0}$, the bulk electron density, for $z \leq -a/2$, and it goes *linearly* to zero over the region $-a/2 \leq z \leq a/2$. In this idealized problern, $\varepsilon\,(z)$ will vanish in the surface region, $|z| \leq a/2$, pi-ovided w is below the bulk plasma frequency $w_p = (4\pi n_0 e^2/m)^{1/2}$. For the calculation shown in Fig. 1, we have chosen $\omega = \omega_p/\sqrt{2}$, $\theta_i = \pi/4$, and all field have been expressed relative to the amplitude E_0 of the incident electric field of light, for the sake of convenience.

The purpose of this paper is to explore the modification of the classical singularity in $E^z(z)$ when one takes into account recent ideas about the transverse dielectric response of a metal surface. Wealso wish to point out how our results may be used profitably to understand certain aspects of recent photoemission data, in the direction of the surface normal, for emission from surface sensitive electronic features, e. g., surface states. In the presence of a real surface, Eq.(1) must be modified in two important respects. The dielectric response is given by a nonlocal tensor[2-5] which, after appropriate Fourier transformations, can be expressed as $\overleftrightarrow{\varepsilon}(z,z')$ becomes a diagonal 'tensor which, however, is anisotropic[6], i.e.,

$$\varepsilon^{xx}_{\vec{Q}\to 0,\omega}(z,z') = \varepsilon^{yy}_{\vec{Q}\to 0,\omega}(z,z') \neq \varepsilon^{zz}_{\vec{Q}\to 0,\omega}(z,z') \ .$$

In the long-wavelength limit, then, the boundary condition becomes a straightforwerd generalization of Eq. (1), viz.

$$\int \varepsilon^{zz}_{\vec{Q}\to 0,\omega}(z,z') \, E^{z}_{\vec{Q}\to 0,\omega}(z')dz'' = \text{constant.} \tag{3}$$

This integral condition is easily recast in terms of the conductivity tensor defined through

$$\overleftrightarrow{\varepsilon}_{\vec{Q},\omega}(z,z') = \delta(z,z')\,\overleftrightarrow{I} + (4\pi i/\omega)\,\overleftrightarrow{\sigma}_{\vec{Q},\omega}(z,z') \ ,$$

and the vector potential $\vec{A}(\vec{r},t)$ where

$$\vec{E}_{\vec{Q},\omega}(z) = \frac{i\omega}{c}\vec{A}_{\vec{Q},\omega}(z)$$

We choose a gauge where the scalar potential $\phi(\vec{r},t)$ identically vanishes, and descriptions in terms of the electric field and the vector potential

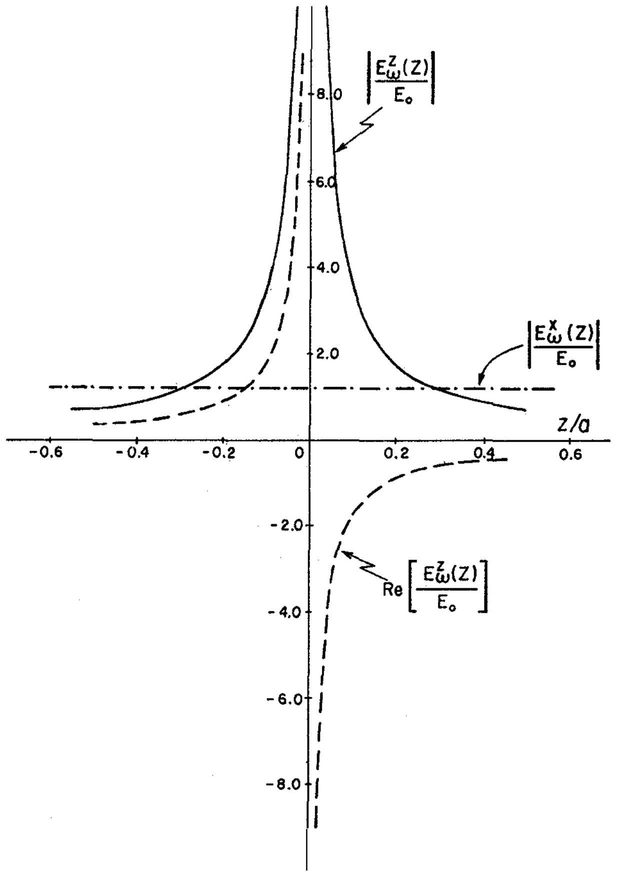

Fig. 1 - Plots of the spatial variation of the real part (dashed curve) and the absolute magnitude (solid curve) of the normal component of the electric field of p-polarized light on reflection from a model semi-infinite system characterized by a local dielectric response varging linearly in the surface region. The dielectric constant is assumed to be $\epsilon_\omega(z) = 1 - \omega_p^2/\omega^2$ for $z \leq -a/2$; $\epsilon_\omega(z) = 1 - \omega_p^2/\omega^2\ 1/2 - z/a$, for $|z| \leq a/2$; and $\epsilon_\omega(z) = 1$ for $z \geq a/2$. The frequency is chosen to be $w = \omega_p/\sqrt{2}$, while θ_i = angle of incidence = $\pi/4$. Also shown as the dash-dotted curve is the z-dependence of the magnitude of the electric field component parallel to the surface in the same problern. All electric fields are expressed relative to E_0, the amplitude of the electric field of incident light.

are equivalent. To evaluate the constant in Eq.(3), we imagine a point Z inside the metal far from the surface (z=0) and yet $|Z| << h$, such that for $z \lesssim Z$, the electric field assumes its bulk form, i.e., it describes a wave trarismitted into the bulk. In this region the dielectric tensor must be isotropic[6-7] and short-ranged [4], and will lead to the long-wave-length dielectric constant of the bulk, $\varepsilon(0,\omega)$ when integrated over one of its variables. Taking advantage of the short-ranged nature of the non-local response, we arrive at the boundary condition derived by Feibelman,[5]

$$A_{\omega}^{z}(z) + \frac{4\pi i}{\omega} \int \sigma^{zz}_{\vec{Q}\to 0,\omega}(z,z') \quad A_{\omega}^{z}(z')dz' = \varepsilon(0,\omega)\ A_{\omega}^{z}(Z) \ . \qquad (4)$$

Here we have suppressed the momentum argument of the vector potential, $\vec{Q}\to 0$. for simplicity.

. Instead of solving the integral equation (4) numerically for model potentials describing the metal, as was done in previous -work [4,5], we shall solve the the equation approximately in an attempt to understand how the nature of the classical singular; ty in $A^{z}(z)$ changes in the presence of a real surface. To this end we assume that the metal can be represented by a semi-infinite square well, i.e., that its electrons may be regarded as non-interacting moving quantum-mechanically in the potential $V(\vec{r}) = V(z) = -V_0\ \theta(-z)$. Physically this means that we ignore crystallinity of the solid and regard the metal as a semi-infinite jellium with the boundary condition of specular reflection at the surface. Also in the conductivity tensor, fhis implies using the Random - Phase Approximation (RPA)[6] in treating the electron-electron interaction. Electrons populate all states of the well up to the Fermi energy E_F, and the bulk electron density $n_0 = k_F{}^3/3\pi^2$ can be expressed in terms of the Fermi momentum K_F. The work function of the metal is given by $\phi = V_0 - E_F$, while the long-wave-length dielectric function assumes the familiar form $\varepsilon(0,\omega) = 1 - \omega_p{}^2/\omega^2$ in terms of the bulk plasma frequency. It is convenient to express the vector potential in Eq. (4) in dimensionless form, either by taking its ratio with $A_{\omega}^{z}(Z)$ or with A_0, the amplitude of the vector potential associated with the incident wave. We define the dimensionless functions

$$\bar{A}_\omega(z) = A^z_\omega(z)/A^z_\omega(Z) \quad , \tag{5a}$$

and

$$\tilde{A}_\omega(z) = A^z_\omega(z)/A_0 \quad . \tag{5b}$$

The former function goes to unity deep into the bulk, $\bar{A}_w(z \to -\infty) = 1$, while the latter is more physical in the sense that it is related to the amplitude for photoexcitation. Eq. (4) shows that

$$\bar{A}_\omega(z) + \frac{4\pi i}{\omega}\int \sigma^{zz}_{\vec{Q}\to 0,\omega}(z,z')\,\bar{A}_\omega(z')dz' = (1-\omega_p{}^2/\omega^2), \tag{6a}$$

and

$$\tilde{A}_\omega(z) = \bar{A}_\omega(z)\,\tilde{A}_\omega(Z) \quad . \tag{6b}$$

We solve Eq. (6a) approximately by assuming that $\bar{A}_\omega(z')$ is smooth and varies weakly over the range of non-locality of $\sigma^{zz}(z,z')$. Then the function can be evaluated at any convenient - point over the range of non-locality of conductivity, and taken out of the integral sign. The components of the relevant conductivity tensor for the square well model have been worked out with - in the RPA in a previous paper [6], where it is shown that

$$\int \sigma^{zz}_{\vec{Q}\to 0,}(z,z')dz' = \frac{i\,n_0(z)\,e^2}{m\,\omega} + \Delta\sigma_\omega(z) \quad , \tag{7a}$$

$$\Delta\sigma_\omega(z) = \frac{i\,n_0\,e^2}{m\,\omega}F_\omega(z) \tag{7b}$$

$$\frac{i\,e^2\hbar^2}{\omega m^2}\;\frac{V_0}{\hbar\omega}\sum_{\vec{K}\kappa} f(\varepsilon_{\vec{K}\kappa})\;\phi_\kappa(0)\;\{\frac{\partial}{\partial z}G^+(z,0;\varepsilon_\kappa+\hbar\omega)$$

$$x\;\phi_\kappa(z) - G^+(z,0;\varepsilon_\kappa+\hbar\omega)\frac{\partial\phi_\kappa(z)}{\partial z} - \frac{\partial}{\partial z}G^+(z,0;\varepsilon_\kappa)\;\phi_\kappa(z)$$

$$+ G^+(z,0;\varepsilon_\kappa)\frac{\partial\phi_\kappa(z)}{\partial z} + G^-(0,z;\varepsilon_\kappa-\hbar\omega)\frac{\partial\phi_\kappa(z)}{\partial z} -$$

$$- \frac{\partial}{\partial z} G^{-}(0,z;\varepsilon_{\kappa} - \hbar\omega)\ \phi_{\kappa}(z) - G^{-}(0,z;\ \varepsilon_{\kappa})\ \frac{\partial \phi_{\kappa}(z)}{\partial z} +$$

$$+ \frac{\partial}{\partial z} G^{-}(0,z;\ \varepsilon_{\kappa})\ \phi_{\kappa}(z)\} \ . \tag{7c}$$

In the last equation, $f(\varepsilon_{\vec{K}\kappa})$ stands for the Fermi occupation function of an electroii of momentum $\vec{K}$ in the xy-plane and quantum nurnber κ formotion along z, and $G^{\pm}$ represent one-dimensional Green's functions of the semi--infinite square well probelm with the appropriate boundary conditionsof outgoing oi- incoming waves at infinity. The dimensionless function $F_{\omega}(z)$ has been introduced to describe the shape of $\Delta\sigma_{\omega}(z)$ and its rea1 and imaginary parts are plotted for certain choices of w in Ref.6. The approximate solution of the integra1 equation for the vector potential near a surface is then

$$\bar{A}_{\omega}(z) = \frac{(1 - \omega_p{}^2/\omega^2)}{1 - (\omega_p{}^2/\omega^2)\ (n_0(z)/n_0 + F_{\omega}(z))} \tag{8}$$

We can compute $\bar{A}_{\omega}(z)$ simply by calculating $n_0(z)$ and $F_{\omega}(z)$ for the model of metal discussed above.

Equation (8) shows that the classical singularity in $A^{z}_{\omega}(z)$ can be recovered in accordance with Eq. (1) by setting $F_{\omega}(z) = 0$, and the singularity occurs when $n_0(z)/n_0 = w^2/w_p{}^2$. This result should be expected because $F_w(z)$ measures the anisotropy in the dielectric response caused by the surface, which is a quantum mechanical effect. The correction vanishes far from the surface, i.e. $F_{\omega}(z) = 0$ as $|z| \to \infty$, and physically it can be related to photon absorption by the surface potential variation[6].

Since $F_{\omega}(z)$ is in general complex, the presence of the surface in a real calculation has the twin effects of shifting the location of the singulerity and making the vector potential finite everywhere, so that an ertswhile singularity is now turned into a peak. This behavior is illuçtrated in Figs. 2 and 3, where we have plotted the real and imaginary parts of $\bar{A}_{\omega}(z)$ as well as the modulus $|\bar{A}_{\omega}(z)|$ against $K_F z$ when $\hbar\omega = 5.0$ eV. For oui- calculation we choose V_0 = 10.7 eV and ϕ = 4.5 eV, as in Ref. 6, to describe the metal. In this model, $\hbar\omega_p$ = 9.813 eV, K_F = 1.2748 Å^{-1}, and the expected location of the singularity in F (z) when $z = 0$ is indicated by an arrow in Fig.3. The important feature to note is the peak in $|\bar{A}_\omega(z)|$ close to the surface, which occurs in close vicinity of the classical singularity and is, indeed, a manifestation of the latter in the present calculation. The other peaks in $|\bar{A}_\omega(z)|$ arise from Friedel oscillations in $n_0(z)$ or from oscillations in $F\omega(z)$ as discuss else-

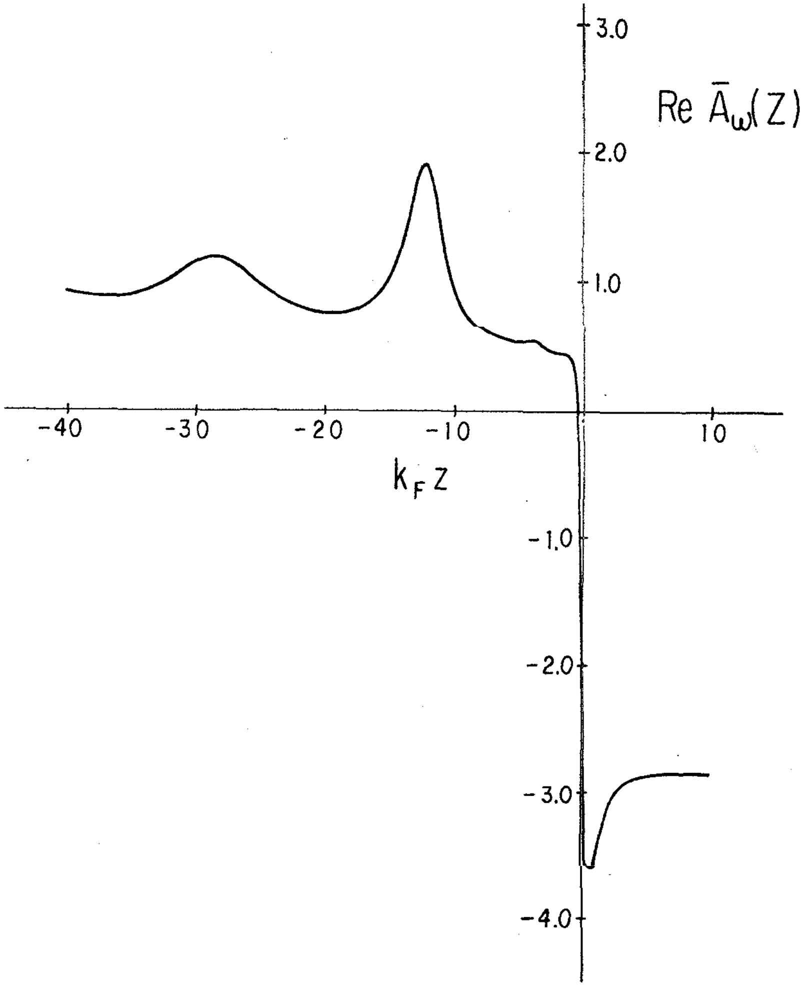

Fig. 2 - The real part of $\bar{A}_\omega(z)$ plotted against $K_F z$ near the surface by solving Eq. (8) with $\hbar\omega$ = 5.0 eV. The metal is represented by a semi-infinite square well occupying the region $z \leq 0$, having a well-depthof 10.7 eV and a work function of 4.5 eV. For this model, $\hbar\omega_p$ = 9.813 eV and K_F = 1.275 Å^{-1}.

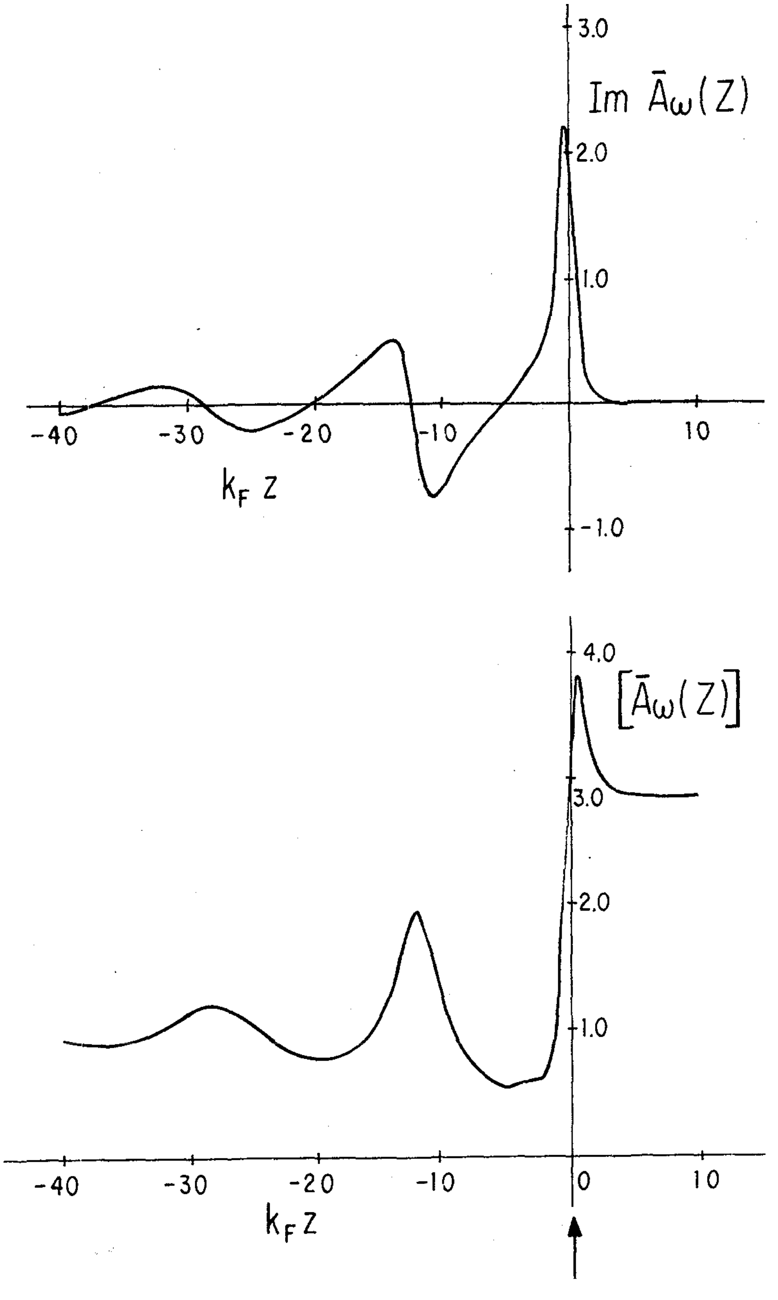

Fig. 3 - Graphs of $Im\ \bar{A}_\omega(z)$ and $\bar{A}_\omega(z)$ versus $K_F z$ for $\hbar\omega$ = 5.0 eV (cf. Eq.8). The parameters describing the metal are given in the caption for Fig. 2. The vertical arrow denotes the expected location ofthe classical singularity.

where[6]. Similar peaks have been found by Feibelman[4] in a more complete calculation of $\bar{A}_\omega(z)$ close to the surface. We believe that ours is the first effort to give a physical interpretation to the origin of these surface peaks, and that it is the correct one.

As the frequency of light is increased the classical singularity (for $\omega < \omega_p$) moves toward the interior of the solid. Fig. 4 shows the results of our calculation for $|\bar{A}_\omega(z)|$ when $\hbar\omega$ = 6.0 and 7.5 eV, and we clearly find that the surface peak in $|\bar{A}_\omega(z)|$ moves across the surface and into the solids as the frequency is raised. Once again, vertical arrows in the figure indicate the expected location of the singularity if surface-induced quantum effects are ignored. Finally in Fig.5, we show results of calculation based on Eq. (8) when w exceeds w_p and the classical singularity is no longer expected. For $\hbar\omega$ = 10 eV ($\gtrsim \hbar\omega_p$), the light field in seen to penetrate a great distance into the solid, and the peak near the surface has all but disappeared. For $\hbar\omega$ = 12.5 eV, however, there appears to be a prominent peak in $|\bar{A}_\omega(z)|$ inside the solid $\sim 2k_F^{-1}$ from the surface. This peak occurs because of Friedel-type oscillations in $n_0(z)$ in Eq. (8). Its location is essentially frequency-independent in our calculation, while its strength rises at first with frequency when $\omega \gtrsim \omega_p$, but then falls sharply. In the rest of the paper we confine our attention to the frequency region $\omega > \omega_p$.

We next try to assess the reality and physical significance of the peak in $|\bar{A}_\omega(z)|$ close to the surface with the help of the following argument. The rapid variation of the magnitude of the normal component of the electric field near a metal surface arises from refraction through the boundary condition of Eq. (3). The large magnitude and rapid variation of $|\bar{A}^z_\omega(z)|$ at the surface suggest that refraction of light may, under certain circumstances, lead to an enhancement of coupling of light to surface electronic features, e.g., surface states or adsorbate energy levels. The perturbing Hamiltonian produced by light and responsible for photoemission is known to be

$$H_{\text{pert}} = \frac{e}{2mc}\left[\vec{p}\cdot\vec{A}_{\vec{Q},\omega}(z)\, e^{i\vec{Q}\cdot\vec{\rho}} + e^{i\vec{Q}\cdot\vec{\rho}}\,\vec{A}_{\vec{Q},\omega}(z)\cdot\vec{p}\right] e^{-i\omega t} \qquad (9)$$

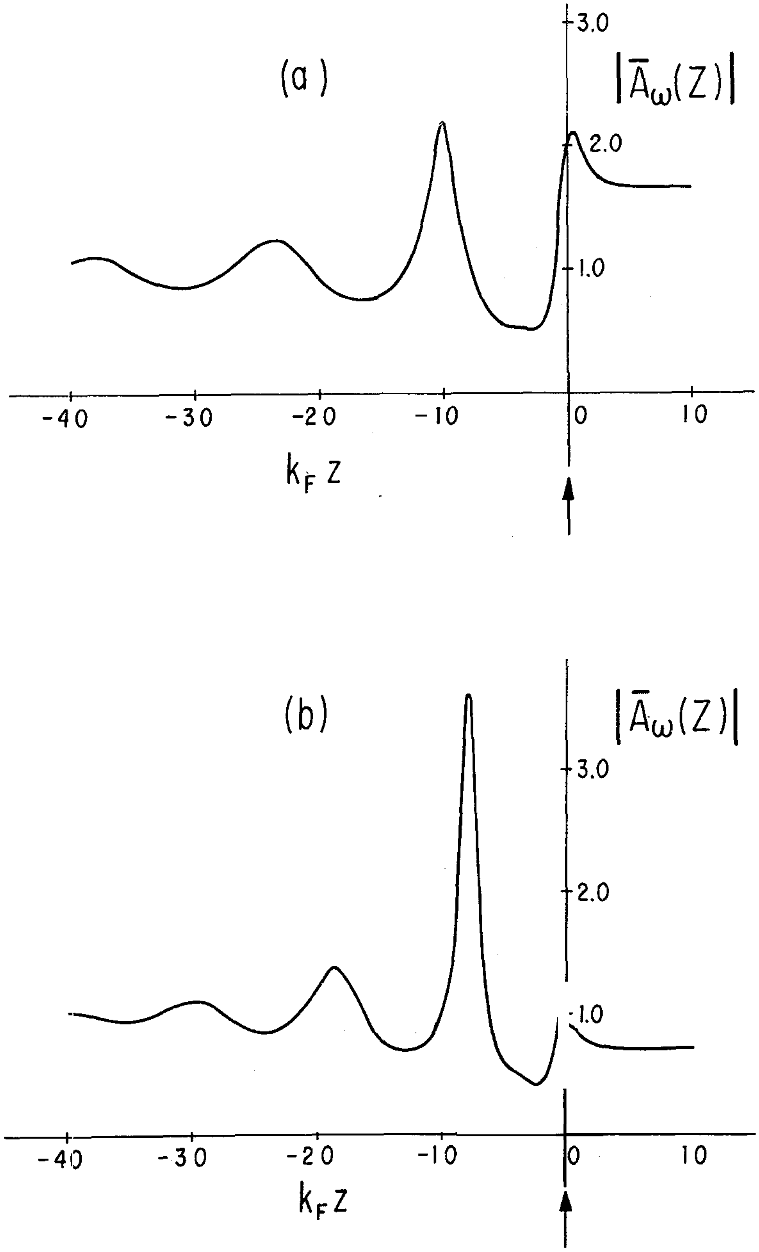

Fig. 4 - Plots of the absolute magnitude of $\bar{A}_{\omega}(z)$ against $K_F z$ for (a) $\hbar\omega = 6.0$ eV and (b) $\hbar\omega = 7.5$ eV obtained by solving Eq. (8). Pararneters of the metal are given in the caption for Fig. 2, and vertical arrows shown in this figure indicate the expected location of the classical singularity.

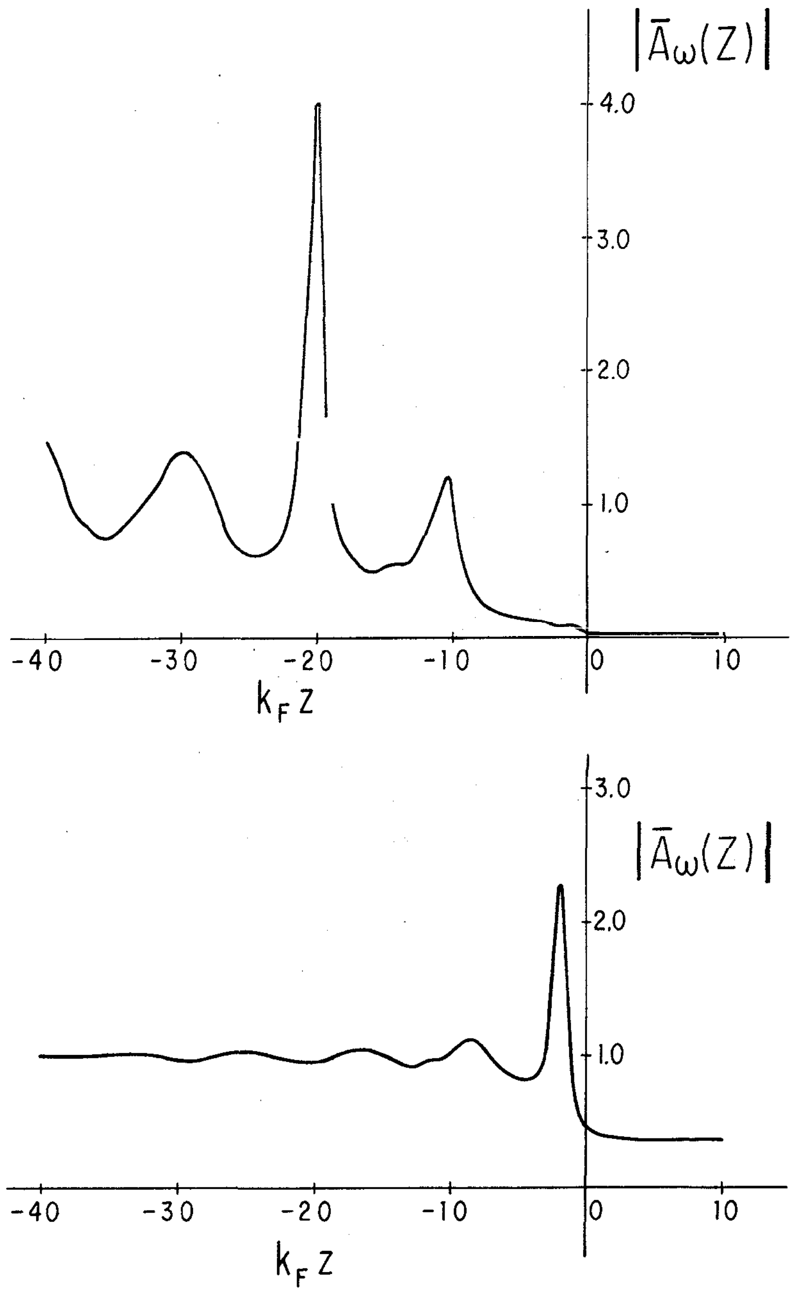

Fig. 5 - Plots of $|\bar{A}_{\omega}(z)|$ versus $K_F z$ for (a) $\hbar\omega$ = 10.0 eV and (b) $\hbar\omega$ = 12.5 eV, both greater than the plasmon energy $\hbar\omega_p$ = 9.813 eV. See the caption for Fig. 2 for the parameters describing the metal in the calculation.

For photoemission in the direction of the surface normal, the *amplitude* (i.e., the square root of the differential cross section) will depend on the matrix element of $p^z\, A^z_\omega(z)/A_0$ between the initial and final electronic state-vave functions, i.e., it will depend on the matrix ofthe quantity $\tilde{A}_\omega(z)$ defined in Eq.(5b). Recalling the formula of Eq.(6b) and the results expressed in Figs. 2-5, it is plausible to argue that if there is a peak in $\tilde{A}_\omega(z)$ occuring within one or two Fermi wavelengths of the surface, then it will couple strongly to a surface state, Arguing in the same spirit, it also appears likely that the height of the surface peak in $|\tilde{A}_\omega(z)|$ will be a crude measure of the strength of photoemission from the surface state, its square being relate to the differential photoemission cross section along the surface normal. Thus from our calculated surface peaks in $|\tilde{A}_\omega(z)|$, we can draw certain general conclusions about photoemission from surface state, provided we can determine $|\tilde{A}_\omega(Z)|$. Note that our conclusions will not be based on a self-consistent theory where refraction of light should occur at a metal surface having a surface state. Rather it will be more in the spirit of the early theory of surface photoelectric effect[8,9] where one considers a surface but neglects refraction entirely. Here we take refraction at jellium surface into account and use it to predict the strength of normal photoemission from a surfece state. The determination of $|\tilde{A}_\omega(Z)|$ inthe long wavelength limit posess no great difficulty. It follows from Eqs. (4) and (5b) that

$$\tilde{A}_\omega(z\to\infty) = \varepsilon(0,\omega)\, \tilde{A}_\omega(Z) \quad , \tag{10}$$

i.e., the boundary conditions is the same as the classical boundary condition except that the surface here is diffuse rather than sharp. This implies that $|\tilde{A}_\omega(Z)|$ will be given correctly by the magnitude of the z--component of the A-field just inside the solid for the classical problem of refraction of p-polarized light at an ideally sharp reflecting surface. (The component of $\vec{A}_\omega(z)$ parallel to the surface is of course knorwn to be constant across it.) In Fig. 6, we have plotted $|\tilde{A}_\omega(Z)|$ versus ω/ω_P by solvirg the problem of refraction at a sharp surface separating vacuum from jellium of dielectric constant $\varepsilon(0,\omega)$. The angle of incidence θ_i has been chosen to be 45°. Using this result in conjunction with our previous calculation for $|\tilde{A}_\omega(z)|$, for any frequency. Figure 7 shows the variation of $|\tilde{A}^{peak}_\omega|$ the rtrength of the surface peak in $|\tilde{A}_\omega(z)|$,

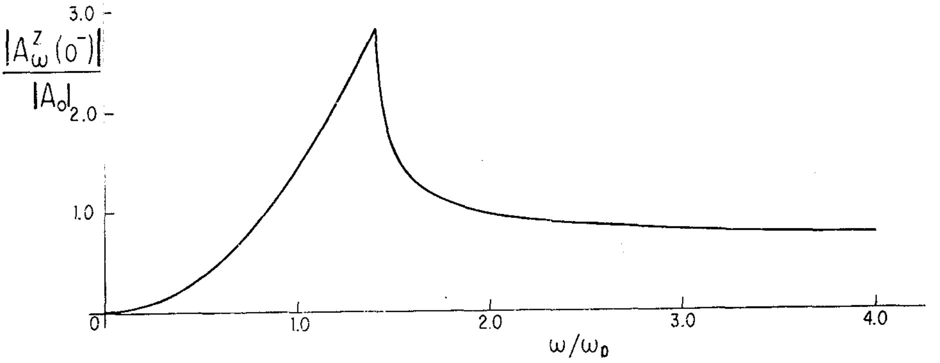

Fig. 6 - Absolute magnitude of $A^z(0^-)$, the normal component of the vector potential just inside the surface, expressed relative to the amplitude A_0 of the incident vector potential and plotted against ω/ω_p in the refraction of p-polarized light at a sharp boundary (z=0) separating vacuum ($z \geq 0$) frorn jellium ($z \leq 0$) of dielectric constant $\varepsilon(0,\omega) = 1 - \omega_p^2/\omega^2$. The angle of incidence θ_i is chosen to be $\pi/4$. Eq. (10) shows that this function should represent A (Z). (See argument in text).

for any frequency w. Figure 7 shows the variation of $|\tilde{A}_\omega^{peak}|$ as a function of ω for $\omega \leq \omega_p$. As argued previously, this curve ought to mirror the variation of the amplitude of photoemission in the normal direction, froma surface state, with the frequency of ligth. It is clear from this figure that $|\tilde{A}_\omega^{peak}|$ goes precipitously to zero as ω approaches ω_p, thus suggesting that photoemission from a surface state in the normal direction with p-polarized light must be very weak near the plasma frequency. Evidence for this kind of behavior has been reported experimentally[10,11] for photoemission from the surface state of $W(100)$. We therefore, conclude that the peaks in $|\tilde{A}_\omega(z)|$ discussed in this paper and lying close to the surface are indeed real, that they arise from the effect of refraction at a metal surface, and that they may be of importance in understanding the frequency dependence of photoemission cross section from surface states on a metal surface, especially for light frequency close to the plasma frequency

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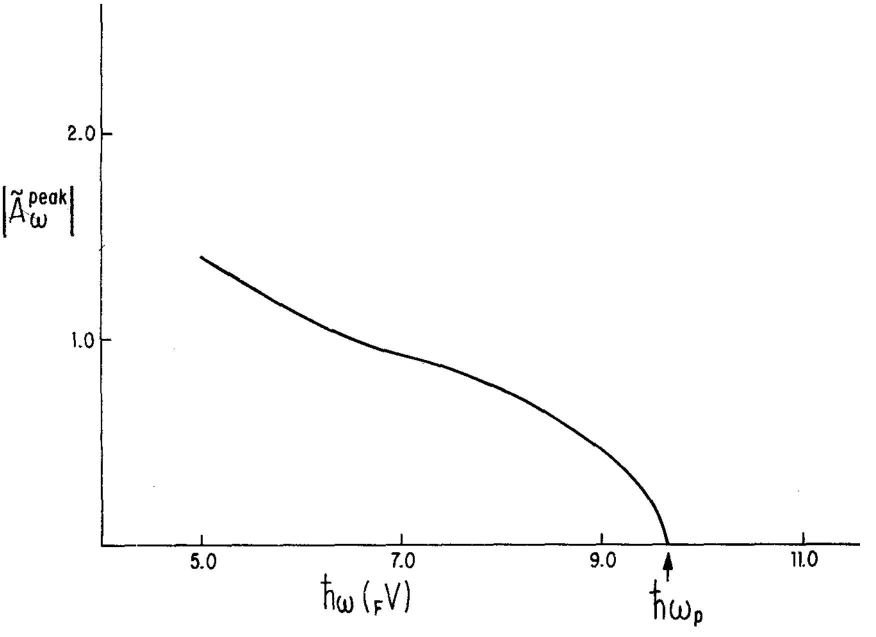

Fig. 7 - Plot of $|\tilde{A}_\omega^{peak}|$, the strength of the surface peak in $|\tilde{A}_\omega(z)|$, as a function of light frequency ω for $\leq \omega_p$.

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