Extension of Makinson's Theory of Photoelectric Emission to a Periodic Potential

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The results of Makinson's treatment of the transition probability for photoelectric emission for a free-electron model has been extended to Bloch wave functions in a periodic field. The particular application of these results to the case of electrons at the top of a filled band has been developed, thereby filling in some of of the details of the preceding paper.

MAKINSON[1] has shown that for a free-electron metal the probability for photoelectric emission for the kth electron is given by the product of D the transmission coefficient of the surface barrier for the excited electron, and $E(\mathbf{k}, \nu)$ which plays the role of an excitation function and determines the probability that the kth electron absorbs a photon of frequency ν. This function is proportional to the square of the component of the incident light normal to the surface and to the square of a particular integral which is linear in the wave function of the unexcited electron. This integral $N(\mathbf{k}, \nu)$ is given according to Makinson's notation by

$$N(\mathbf{k}, \nu)=\int_{-\infty}^{\infty}(\chi_r\phi_k'-\chi_r'\phi_k)/\{\epsilon_1+i\epsilon_2\}dx, \quad (1)$$

where ϕ_k is the wave function for the unexcited electron, χ_r is an auxiliary wave function with an energy corresponding to that of the electron after a photon of frequency ν has been absorbed, and ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric constant. The direction of x is taken to be perpendicular to the surface ($x=0$) of the metal.

Though Makinson's original treatment was limited to a free-electron model, this limitation is not an essential one. The purpose of the present paper is to apply the development to the corresponding wave functions appropriate to the problem of photoelectric absorption at the surface of an insulator or semiconductor. In such physical situations, the periodicity of the potential inside the solids cannot be ignored and the wave function cannot be represented simply by plane waves. The more generalized functions necessary here can be expressed in terms of a double Fourier series in the primitive translational vectors of the surface whose coefficients are functions of x. All functions used in calculating the excitation function for a particular electron have the same properties with respect to the surface translations.

For the wave function of the unexcited electron, one uses expressions equivalent to those in Eqs. (8), (10), and (11) of the preceding article.[2] Inside the crystal one has

$$\phi_k(\mathbf{r})=\exp(i\mathbf{k}_\rho\cdot\boldsymbol{\varrho})\sum_m\exp(-i\mathbf{K}_m\cdot\boldsymbol{\varrho}) \times[\sum_n(A_{nm}\exp\{-i(L_n+k_x)x\} +A_{nm}^*\exp\{i(L_n+k_x)x\})+S_m(x)]. \quad (2)$$

Nere x measures distance perpendicular to the surface and $\boldsymbol{\varrho}$ is a vector lying in the plane of the surface. The symmetry of the wave function with respect to the surface translations is determined by $\mathbf{k}_\rho$. The translation vectors of the lattice reciprocal to the surface net are represented by the K_m, and the L_n are $2\pi n$ divided by d, the shortest unit translation perpendicular to the surface. The functions $S_m(x)$ falls rapidly to zero for $x\rightarrow-\infty$ going from the surface into the solid. These functions are required to fit the surface boundary conditions, whereas the A_{nm} are determined by solving the Schrödinger equation for the interior of the solid. Outside the solid for $x>0$ one has, assuming a uniform potential,

$$\phi_k(\mathbf{r})=\exp(-i\mathbf{k}_\rho\cdot\boldsymbol{\varrho})\sum_m s_m\exp(-p_mx-i\mathbf{K}_m\cdot\boldsymbol{\varrho}), \quad (3)$$

where the p_m and s_m are constants.

Similar expressions for the wave functions of the excited electron can be constructed. Inside the solid, one has

$$\theta_k(\mathbf{r})=\exp(-i\mathbf{k}_\rho\cdot\boldsymbol{\varrho}) \times\sum_m\exp(-i\mathbf{K}_m\cdot\boldsymbol{\varrho})[C_m(x)+T_m(x)], \quad (4)$$

where the T_m decrease rapidly going into the crystal and the C_m each represent one or more plane waves of the type $\exp(iqx)$ modulated by a function periodic in d. For a free-electron metal, the value for q was determined uniquely to be $[k_x^2+(8\pi^2m/h^2)\nu]^{\frac{1}{2}}$; but for the more general case under consideration, multiple values of q (even for the same m) may exist which satisfy the conditions for conservation of energy and momentum parallel to the surface. Whether or not such complications occur depends on the complexity of the Brillouin zone structure. Multiple values of q will be most probable for multiple-leaved surfaces in the same energy range. Outside the crystal one has

$$\theta_k(\mathbf{r})=\exp(-i\mathbf{k}_\rho\cdot\boldsymbol{\varrho})[\sum_m B_m\exp i(r_mx-\mathbf{K}_m\cdot\boldsymbol{\varrho}) +\sum_m' t_m\exp(-r_m'x-i\mathbf{K}_m\cdot\boldsymbol{\varrho})]. \quad (5)$$

The unprimed summation includes only those values of surface momentum which leave enough normal energy

[1] R. E. B. Makinson, Phys. Rev. **75**, 1908 (1949).
[2] H. B. Huntington and L. Apker, Phys. Rev. **89**, 352 (1952).

for the electron to escape. The primed summation includes the remaining (larger) values of $\mathbf{K}_\rho$.

The construction of the auxiliary function depends upon the purpose for which it is to be used. To calculate the probability that the electron will escape with particular momentum parallel to the surface $(\mathbf{k}_\rho+\mathbf{K}_1)\hbar$, one takes for inside the solid

$$\chi_r(\mathbf{r})=\exp\{i(\mathbf{k}_\rho+\mathbf{K}_1)\cdot\boldsymbol{\varrho}\}\times[\textstyle\sum_i \exp(-iq_ix)u_i(\mathbf{r})+V(\mathbf{r})], \quad (6)$$

and for outside the solid

$$\chi_r(\mathbf{r})=\exp\{i(\mathbf{k}_\rho+\mathbf{K}_1)\cdot\boldsymbol{\varrho}\}[G_1e^{ir_1x}+H_1e^{-ir_1x}+v(\mathbf{r})]. \quad (7)$$

The summation over i takes care of possible multiple values of q. $V(\mathbf{r})$ has the periodicity of the surface and falls off rapidly toward the interior. The u_i have the periodicity of the lattice and are individually normalized so that the integral of the amplitude squared over the solid gives unity. The function v has the periodicity of the surface and dies off rapidly at large distances from the crystal. The quantity r measures the normal momentum of the escaping electron and can be found from the relation

$$(\hbar^2/2m)[(k_\rho+K_1)_2+r_1{}^2-k_\rho{}^2-k_x{}^2]=h\nu-\epsilon_0, \quad (8)$$

where ϵ_0 is the energy difference from the bottom of the filled band to the vacuum level and the energy level of the kth electron is approximated by the free-electron formula.

According to Makinson's Eq. (4), the relation between ϕ and θ can be expressed as

$$\nabla^2\theta_k+\{r^2+(k_\rho+K_1)^2-(8\pi^2m/h^2)U_k(r)\}\theta_k = -(4\pi ie/ch)\{a_x\phi_k'+i\phi_k(a_yk_2+a_zk_3)+\tfrac{1}{2}\phi_ka_x'\}. \quad (9)$$

$U_k(\mathbf{r})$ is the periodic potential of the lattice as referred to the vacuum level. The a_x, a_y, and a_z are the components of a vector field equal to the amplitude of the time-varying vector potential of the incident light. One multiplies Eq. (9) through by χ_r and integrates over x, y, and z using an extinction factor $e^{\Delta x}$ inside the solid, where Δ is positive. Two applications of Green's theorem to the left side of Eq. (9) so modified reduces it to the sum of a volume integral, which vanishes by virtue of the fact that χ_r is a solution of the Schrödinger equation for the excited electron, and a surface integral over the boundary of our space. The part of the surface integral over the x–y and x–z planes vanishes if one employs the usual periodicity requirements as boundary conditions for $\exp(-i\mathbf{k}_\rho\cdot\boldsymbol{\varrho})$. At the surface $x=-\infty$, the integral vanishes because of the extinction factor. At $x=+\infty$, one is left with only $2ir_1B_1H_1$ per unit area from the surface integral. For the volume integral on the right, the terms involving a_y and a_z give a negligible contribution, and a_x is inversely proportional to $\epsilon_1(x)+i\epsilon_2(x)$, where we have assumed that the dielectric constant is independent of y and z. The integrations over y and z can now be carried out making use of the orthogonality of factors containing different $\mathbf{K}_\rho$. The remaining integration over x becomes (after integration by parts) proportional to a modified form of Eq. (1):

$$\int_{-\infty}^{\infty}\textstyle\sum_m(\chi_{rm}\phi_{km}'-\phi_{km}\chi_{rm}')/[\epsilon_1(x)+i\epsilon_2(x)]dx. \quad (10)$$

Outside the solid, there is only one term in the summation over m, ϕ_{k1} is $s_1\exp(-p_1x)$, and χ_{r1} is the square bracket term in Eq. (7). Inside the solid, the θ_{km} are the square bracket terms in Eq. (2) and the χ_{rm} are the mth Fourier components of the expressions in square brackets in Eq. (6).

For the case where there is only one q_i, Makinson's results obtain practically unmodified [$(M(\mathbf{k},\nu)$ is represented by Eq. (10) rather than (1)]. With multiple values for q, the transmission coefficient of the barrier is no longer simply defined. One can extend the Makinson formalism to these cases by introducing a $\bar{D}$, defined as the average transmission coefficient for equal flux into each of the f states with different q, and an average value for q namely $\bar{q}$. As a result the quantity D/q which appears in Makinson's (7a) is replaced by $f\bar{D}/\bar{q}$. Since it is customary to treat electrons excited to the conduction band as essentially free, the case of multiple q's is probably physically unimportant.

From the standpoint of physical interest also, attention should be centered on transitions for minimum $(\mathbf{k}_\rho+\mathbf{K}_m)$, since there is no experimental evidence of electrons coming off with large components of momentum parallel to the surface.

Our main concern in extending the Makinson treatment to Bloch-type wave functions is to apply it to the electrons at the top of a filled band. The preceding paper[2] was given to the consideration of this problem and it is convenient to use its expressions for ϕ_k as given in Eqs. (8), (10), and (11) of reference 2. The most significant change is that there $\mathbf{k}$ refers to the wave number vector of the hole rather than of the electron as in Eqs. (2) and (3) of this paper. For states near a zone boundary, the additional relation given by Eq. (9) of reference 2 also holds approximately. It has been shown that for small k_x the s_m, the S_m and $(1-A)$ are proportional to k_x (unless an accidental resonance exists). Consequently every part of ϕ_k is either directly proportional to k_x or contains a factor $(1-A)\sin(k_xx)$. Those with the $\sin(k_xx)$ factor give contributions proportional to k_x after the integration over $x<0$ in (10) has been carried out. It follows that $M(\mathbf{k},v)$ will be proportional to k_x, and the transition probability for photoelectric emission from the top of the band is proportional to $k_x{}^2$. Consequently, the transition probability averaged over an equi-energy contour in k space is proportional to the hole energy, and the contribution to the photocurrent from states in an infinitesimal shell at such a contour will be proportional to the $\frac{3}{2}$ power of the hole energy. This result holds for elliptical as well as spherical energy contours.

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