appreciably from its maximum value. The high scattering rate on the necks may also account for the heavy damping of the rosette-orbit oscillations, since this orbit is known to cross four necks.

V. CONCLUSIONS

The magnetoacoustic effect is a bulk measurement in a metal sample, so that surface effects need not be considered either in performing the experiment or in the interpretation of the results. In our relaxation-time studies, this is an advantage by comparison with methods based on cyclotron resonance, where the interaction occurs at the surface of the metal. On the other hand, small-angle scattering is not as effective in the magnetoacoustic effect as in AKCR, so it is necessary to restrict observations to high values of the harmonic index n in order to unambiguously determine the total electron phonon scattering rate. It is not clear that this limiting case has been achieved in the present work.

In spite of the aforementioned uncertainties, we believe that the magnetoacoustic effect has the potential for becoming a precision tool in studies of the electron scattering process. This potential will be realized more fully if some of the intuitive arguments we have been forced to rely upon can be justified by formal analysis.

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Scattering Effects in Photoelectric Emission from Solids. I*

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A simple model of photoelectric emission is solved essentially exactly. The model consists of a one-dimensional solid whose free-electron-like conduction band is cut off by a potential step representing the surface. Inside are sparse random local elastic scattering centers. The rate equations of Kane are derived rigorously, and hence expressions are obtained for the number of photoelectrons which escape with and without scattering as a function of the mean free path, the electromagnetic penetration depth, and the transmission coefficient of the surface barrier.

I. INTRODUCTION

The photoelectric effect is a powerful experimental tool for probing the electronic states of solids. Hopefully one can use it to gain information about the electronic density states of the bulk material. Two effects interfere with this aim: (a) Photoelectrons may originate near the surface where their initial wave function differs substantially from its bulk value; and (b) photoelectrons may scatter a number of times before emerging from the surface. The first effect can arise from the distortion of "band" wave functions near the surface, as recently discussed by Ashcroft and Schaich[1] in a model calculation, or from the presence of localized surface states of the type recently calculated in Cu by Forstmann and Heine[2] to explain some earlier puzzling data. The second effect has been studied phenomenologically by Berglund and Spicer[3] and with a phenomenological Hamiltonian by Sutton.[4] Here we treat the second effect from first principles, but in a simplified model.

Recently Mahan[5] suggested that it might be possible to alleviate these two impediments by measuring the angular distribution of photoelectrons from a perfect crystal. This can only be true if a significant fraction of the photoelectrons emerge without having been scattered; here we calculate this fraction as a function of the mean free path, the electromagnetic penetration depth, and the transmission coefficient of the surface.

In practice, inelastic scattering is probably most important. Here we treat only elastic scattering, because it provides a simple model problem that can be solved exactly essentially, and perhaps the beginnings of a theory for the more realistic case. Actually, to the extent that the energy change per collision is a small fraction of the initial energy, our results for the fraction of photoelectrons escaping with and without scattering should be extendable to inelastic collisions.

The remainder of this section will be devoted to a general formulation of the problem. The model will be defined during the course of the development. In Sec. II the Green's function for the model will be calculated. In Sec. III the vertex function, and hence the final expression for the photocurrent will be obtained. It is shown that the equation for the vertex function, after suitable approximations, is the same as a classical rate equation written down intuitively by Kane.[6]

We begin with the formalism for the full three-dimensional case and specialize to one dimension later. We wish to calculate the distribution function $f(\vec{p}, \vec{r}, t)$, that is, the density of particles of momentum $\vec{p}$ in the vicinity of space point r and time t. Eventually we will take the asymptotic limit $r \to \infty$, that is, we measure the photoelectrons a long way outside the sample. Quantum mechanically, the distribution function is defined by

$$f(\vec{p}, \vec{r}, t) = \int d^3x\, e^{-i\vec{p}\cdot\vec{x}} \langle\langle \psi^\dagger(\vec{r} - \tfrac{1}{2}\vec{x}, t)\, \psi(\vec{r} + \tfrac{1}{2}\vec{x}, t) \rangle\rangle , \tag{1}$$

where $\langle\langle \cdots \rangle\rangle$ represents the actual (nonequilibrium) statistical average. At $t = -\infty$ the system is taken to be in thermal equilibrium before the vector potential $\vec{A}(\vec{r}, t)$ of the incident photons is applied. The formal evaluation and perturbation theoretic expansion of such expressions is standard.[7] In the interaction representation, the average is expressed as

$$\langle\langle \psi^\dagger(x, t)\, \psi(x', t) \rangle\rangle = \langle v^{-1}(t)\, \psi^\dagger(x', t)\, \psi(x, t)\, v(t) \rangle , \tag{2}$$

where $\langle \cdots \rangle$ represents the thermal average according to the unperturbed Hamiltonian H (ground-state expectation value in our case, since we assume that $T = 0$), and $v(t)$ is the ordered exponential

$$v(t) = T \exp\left[-i \int_\infty^t dt\, d^3r\, \vec{j}(\vec{r}, t) \cdot \vec{A}(\vec{r}, t)\right] , \tag{3}$$

where j is the current density operator.

Now, clearly, if $|0\rangle$ is the ground state, then

$$\lim_{r \to \infty} \psi(\vec{r}, t) \,|\, 0\rangle = \lim_{r \to \infty} \langle 0 |\, \psi^\dagger(\vec{r}, t) = 0 , \tag{4}$$

so that the first-order terms in H_1 in the expansion of (2) vanish, and to second order one obtains [using (4)]

$$f(\vec{p}, \vec{r}, t) = \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 \int d^3r_1 \int d^3r_2 \int d^3x\, e^{-i\vec{p}\cdot\vec{x}}$$
$$\times \vec{A}(\vec{r}_1, t_1) \cdot \langle\, \vec{j}(\vec{x}, t_1)\, \psi^\dagger(\vec{r} - \tfrac{1}{2}\vec{x}, t)$$
$$\times \psi(\vec{r} + \tfrac{1}{2}\vec{x}, t)\, j(\vec{x}_2, t_2) \rangle \cdot A(\vec{r}_2, t_2) . \tag{5}$$

The total photocurrent density, as opposed to its momentum decomposition above, is given by[8]

$$\vec{j}(\vec{r}, t) = \int \frac{d^3p}{(2\pi)^3}\; 2e(\vec{p} - e\vec{A}) f(\vec{p}, \vec{r}, t) . \tag{6}$$

Substitution of (5) into (6) reduces to Ashcroft and Schaich's[1] Eq. (8) [noting as they do that the second term in (6) can be neglected to this order].

To evaluate (5), one needs the three-particle correlation function

$$\langle \psi^\dagger(1')\, \psi(1)\, \psi^\dagger(2')\, \psi(2)\, \psi^\dagger(3')\, \psi(3) \rangle . \tag{7}$$

The standard perturbation expansions, however, give the three-particle Green's function, that is, the time-ordered expectation value of the same operators. Thus in general, one calculates the time-ordered product, picks the piece corresponding to the time ordering of (7), and analytically continues to other time orderings, so that one can perform the time integrals indicated in (5).

Here we neglect interactions between electrons, so that (7) can be decomposed into products

$$\langle \psi(1)\, \psi^\dagger(2') \rangle \langle \psi(2)\, \psi^\dagger(3') \rangle \langle \psi^\dagger(1')\, \psi(3) \rangle , \tag{8}$$

where we have used (4) to eliminate other possible factorizations [note that (8) is meant to apply only to the asymptotic limit where r_2 and r_2' are very large]. Let

$$G^{>}(\vec{x}, \vec{x}', \omega) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \langle \psi(\vec{x}, t)\, \psi^\dagger(\vec{x}', 0) \rangle e^{-i\omega t} ,$$
$$G^{<}(\vec{x}, \vec{x}', \omega) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \langle \psi^\dagger(\vec{x}', 0)\, \psi(\vec{x}, t) \rangle e^{-i\omega t} , \tag{9}$$

and assume that the vector potential has the form

$$\vec{A}(\vec{x},t)=\vec{A}(\vec{x})e^{-i(\nu+i\eta)t}+\vec{A}^*(\vec{x})e^{i(\nu-i\eta)t}\ , \qquad (10)$$

where η is a positive infinitesimal; then using (8) and performing the time integrals indicated in (5), we see that we will need

$$\int\frac{d\omega}{\pi}\int\frac{d\omega'}{\pi}\int\frac{d\Omega}{\pi}$$

$$\times\frac{G^>(\vec{x}_1,\vec{x}';\ \omega)\,G^>(\vec{x},\vec{x}_2';\ \omega')\,G^<(\vec{x}_2,\vec{x}_1';\ \Omega)}{(\Omega+\nu-i\eta-\omega)(\Omega+\nu+i\eta-\omega')}\ . \qquad (11)$$

There are actually four terms that result from the square of (10), two of them time dependent, but later it will become clear that (11) is the only one which survives in the asymptotic limit.

At this point we describe the model a bit more. We assume a one-dimensional solid, whose conduction band is entirely free-electron-like (parabolic). The surface is described by a potential step at $x=0$ with vacuum for $x>0$. The photons impinge from the right, and are absorbed by the solid in a penetration depth δ, so that

$$A(x)=A\,e^{-x/2\delta} \qquad (12)$$

(The real part of the photon wave vector is negligible in comparison with other oscillatory terms in the problem.) The photons excite electrons of energy ϵ_k from a lower band to the conduction band. The amplitude for this process is the matrix element of the current operator [see (5)], which we take to be given. With no further approximation then we may take the wave function for the lower band to be given by its envelope (i.e., neglect the periodic modulation) because this is all that is important for wave-vector conservation, and any numerical errors can be lumped into the matrix elements which are to be factored out and left unspecified. In any case, the point under investigation in this work is what happens to the electron once it gets into the conduction band, and not how it got there. Except near the surface, the wave function of the lower band can then be taken to be

$$\phi(x)=(2/\pi)^{1/2}\sin(kx+\alpha)\ . \qquad (13)$$

Deviations from (13) near the surface give rise to the surface effect of Ashcroft and Schaich[1] which will not be considered here. The Green's function for the lower band is defined by

$$G(x,x',z)=\int\frac{d\omega}{2\pi}\,\frac{A(x,x',\omega)}{z-\omega}\ , \qquad (14)$$

where $A(x,x',\omega)$ is the spectral function

$$A(x,x',\omega)$$
$$=\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle\psi(x,t)\psi^\dagger(x',0)+\psi^\dagger(x',0)\psi(x,t)\rangle, \qquad (15)$$

and is thus

$$G(x,x',z)=\frac{2}{\pi}\int dk\ \frac{\sin(kx+\alpha)\sin(kx'+\alpha)}{z-\epsilon_k}\ , \qquad (16)$$

so that

$$G^<(x,x',\Omega)=4\int dk\ \sin(kx+\alpha)$$
$$\times\sin(kx'+\alpha)\,\delta(\Omega-\epsilon_k)f(\Omega)\ , \qquad (17)$$

where $f(\Omega)$ is the Fermi function which in our zero-temperature case vanishes for $\Omega>\epsilon_F$ and equals unity for $\Omega<\epsilon_F$, where ϵ_F is the Fermi energy.

We now return to the reduction of (11) and hence (5). Since the Fermi level must be below the vacuum level and since (11) asymptotically vanishes for values of ω or ω' less than the vacuum level, we may replace the $G^>$'s in (11) by the respective spectral densities, so that according to (14), (11) becomes

$$\int\frac{d\Omega}{2\pi}\ G(x_1,x';\Omega+\nu+i\eta)$$
$$\times G(x,x_2;\ \Omega+\nu-i\eta)\,G^<(x_2,x_1',\Omega)\ . \qquad (18)$$

Finally, the substitution of (10), (12), (17), and (18) into (5) with the proviso mentioned earlier that the single-particle current matrix elements M are to be factored out, yields

$$f(p,r,t)=|A|^2\int_{-\infty}^{\infty}dx\,e^{-\vec{p}\cdot\vec{x}}\int_{-\infty}^{0}dx_1\int_{-\infty}^{0}dx_2\int_0^{\infty}dk$$
$$\times|M|^2\frac{2}{\pi}\sin(kx_1+\alpha)\sin(kx_2+\alpha)\,e^{(x_1+x_2)/2\delta}$$
$$\times G(x_1,r-\tfrac{1}{2}x;\ \epsilon_k+\nu+i\eta)$$
$$\times G(r+\tfrac{1}{2}x,\ x_2;\ \epsilon_k+\nu-i\eta)\ . \qquad (19)$$

In writing (19) we have specialized (5) to our one-dimensional case, and have also assumed that δ is much greater than a lattice spacing, so that the factor $e^{(x_1+x_2)/\delta}$ could be factored out of the matrix elements.

II. GREEN'S FUNCTION

We recall now that in our model there is a random distribution of impurity scattering centers in the solid ($x<0$). Therefore, we must take an ensemble average (denoted by $\langle\cdots\rangle_{\text{av}}$) over all impurity distributions. Thus, we need

$$\langle GG\rangle_{\text{av}}=\langle G\rangle_{\text{av}}\langle G\rangle_{\text{av}}+\cdots\ \ . \qquad (20)$$

The difference between the left-hand side of (20) and the first term of the right-hand side is the vertex correction to be calculated in Sec. III. Here we calculate $\langle G\rangle_{\text{av}}$, which we denote for brevity by g.

The average Green's function g satisfies Dyson's equations

$$\left(E \pm i\eta + \frac{d^2}{dx^2} - V(x) \right) g(x, x'; E \pm i\eta)$$

$$= \delta(x - x') + \int d\bar{x}\, \Sigma(x, \bar{x}) g(\bar{x}, x'; E \pm i\eta) \qquad (21a)$$

and

$$\left(E \pm i\eta + \frac{d^2}{dx'^2} - V(x') \right) g(x, x'; E \pm i\eta)$$

$$= \delta(x - x') + \int d\bar{x}\, g(x, \bar{x}; E \pm i\eta) \Sigma(\bar{x}, x') , \qquad (21b)$$

subject to the boundary condition that g vanish as x or $x' \to \pm\infty$. Here the potential $V(x)$ vanishes inside the solid ($x < 0$) and is equal to a constant V_0 outside ($x > 0$). The diagrammatic expansion for the self-energy Σ in terms of the Green's function is well known. We assume that we are in the limit of low density of scatters ($|\Sigma| \ll E$). In this case the diagrams contributing to Σ are indicated in Fig. 1(a); they have the sum

$$\Sigma(x, x') = \int dr\, n(r)\, t_r(x, x') , \qquad (22)$$

where $n(r)$ is the density of scatterers

$$n(r) = n\theta(-r) , \qquad (23)$$

and $t_r(x, x')$ is the scattering matrix for an electron scattering off an isolated impurity located at point r. We make one further simplifying assumption about our model, that the scattering is local, so that $\Sigma(x, x')$ is proportional to $\delta(x - x')$. (This would be rigorously true for impurities with a δ-function potential.) We are thus neglecting any momentum dependence of the scattering. Therefore, since the real part of Σ is negligible in the low-density limit, we have

$$\Sigma(x, x'; E \pm i\eta) = \mp (i/2\tau)\, \delta(x - x')\, \theta(-x) , \qquad (24)$$

where τ is the mean free time:

$$1/2\tau = \mp n |t|^2 \operatorname{Im} g\, (x, x; E \pm i\eta) . \qquad (25)$$

Henceforth we will take τ to be independent of x [but note the θ function in Eq. (24)]. This is not exactly true because (25) contains the true averaged Green's function g rather than the bare Green's function; the latter varies with x in a small region near the surface (unless $E \gg V_0$).

Substitution of (24) into (21) yields a set of equations which are easily, but rather tediously solved for G. The solution is

$$G(x, x'; E - i\eta)$$

$$= \left(\frac{1}{2ib_1} - \frac{1}{i(b_1 + b_2)} \right) e^{ib_1(x + x')} - \frac{1}{2ib_1} e^{-ib_1|x - x'|}$$

for $x < 0$, $x' < 0$

$$= \left(\frac{1}{2ib_2} - \frac{1}{i(b_1 + b_2)} \right) e^{-ib_2(x + x')} - \frac{1}{2ib_2} e^{ib_2|x - x'|}$$

for $x > 0$, $x' < 0$

$$= -\frac{1}{i(b_1 + b_2)} e^{-ib_2 x} e^{ib_1 x'} \quad \text{for } x > 0, \quad x' < 0$$

$$= -\frac{1}{i(b_1 + b_2)} e^{ib_1 x} e^{-b_2 x'} \quad \text{for } x < 0, \quad x' > 0 , \qquad (26)$$

where

$$b_1^2 = E - i/2\tau, \quad b_2^2 = E - V_0 - i\eta , \qquad (27)$$

with $\operatorname{Im} b_1 < 0$ and $\operatorname{Im} b_2 < 0$. The solutions for $G(x, x'; E + i\eta)$ are the complex conjugates of (26). The mean free path l is given by $l = 2E^{1/2}\tau$, and an electron of energy E has a momentum of magnitude $p_1 = E^{1/2}$ inside and $p_2 = (E - V_0)^{1/2}$ outside. Since $1/\tau \ll E$, (27) becomes approximately

$$b_1 \simeq p_1 - i/2l, \quad b_2 \simeq p_2 . \qquad (28)$$

In fact, we may neglect the imaginary parts in (28) altogether, except where they appear in the exponentials in (26). The transmission coefficient T and reflection coefficient R of the surface barrier is

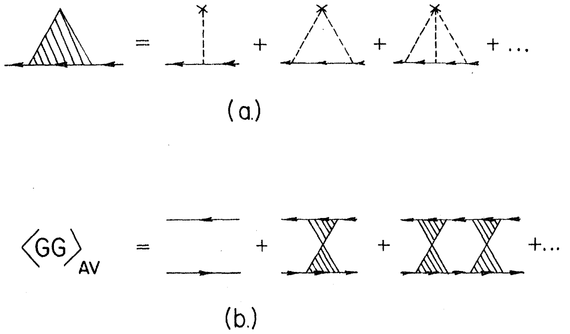
$$R = 1 - T = \left(\frac{p_1 - p_2}{p_1 + p_2} \right) , \qquad (29)$$

so that

$$G(x, x', E - i\eta)$$

$$\simeq -\frac{1}{2ip_1} \left(R^{1/2} e^{i(p_1 - i/2l)(x + x')} + e^{-i(p_1 - i/2l)|x - x'|} \right)$$

for $x' < 0$, $x < 0$



(a)

(b)

FIG. 1. Part (a) shows the diagrams which contribute to the self-energy in the limit of a low density of scattering centers. The solid lines represent the true averaged Green's function g, the dashed lines represent the potential of the scattering center, and the crosses represent the position of a single scattering center, which is to be multiplied by their local macroscopic number density, and integrated over all space. The external g lines are shown only for clarity and are not included in the definitions. Part (b) shows the diagrams which contribute to the average of two Green's functions.

$$\simeq -\frac{1}{2i(p_1p_2)^{1/2}}\; T^{1/2}\, e^{i(p_1 - i/2l)x}\, e^{-ip_2x'} \qquad \text{for } x<0,\ x'>0, \tag{30}$$

plus similar relations for the other cases.

We now evaluate $f(p)$ and hence the photocurrent in the approximation $\langle GG\rangle_{\mathrm{av}} = gg$; that is, we consider only the first term in the diagrammatic summation in Fig. 1(b). The vertex corrections to this will be considered in Sec. III. Physically, then, we will be calculating the contribution to $f(p)$ arising from those electrons emerging from the surface without having been scattered.

Reference to Eq. (19) shows that we will need the quantity

$$\int_{-\infty}^{\infty} d\bar{x}\, \sin(k\bar{x}+\alpha)\, e^{\bar{x}/2\delta}\, g(\bar{x}, r-\tfrac{1}{2}x;\ E-i\eta), \tag{31}$$

which on substitution of (30) becomes

$$\frac{1}{4i}\,\frac{T}{p_1p_2}\,\frac{e^{-i\alpha}}{p_1 - k - i(1/2\delta + 1/2l)}\,\frac{e^{i\alpha}}{p_1 + k - i(1/2\delta + 1/2l)}\,. \tag{32}$$

This is only large when $p_1 \sim k$, since p_1 and k are much larger than $1/\delta$ or $1/l$ and are both defined to be positive; therefore the second term can be neglected so that squaring and substituting into (19) gives

$$f_0(p) = \frac{A^2}{4}\int_0^{\infty} dk\, \frac{\delta(p_2 - p)}{p_2}\,\frac{TM^2}{p_1} \times \frac{1}{(p_1-k)^2 + (1/2\delta + 1/2l)^2}, \tag{33}$$

where we denote this unscattered contribution to $f(p)$ by $f_0(p)$. Again since $1/\delta + 1/l$ is small, we have

$$\frac{1}{(p-k)^2 + (1/2\delta + 1/2l)^2} \simeq \frac{2\pi\delta l}{\delta + l}\,\delta(p_1 - k) = \frac{2\pi\delta l}{\delta+l}\, 2\delta(\epsilon_k + \nu - k^2), \tag{34}$$

so that

$$f_0(p) = \pi A^2 \int_0^{\infty} dk\, \frac{\delta(p_2 - p)}{p}\,\frac{TM^2\delta l}{\delta + l}\,\delta(\epsilon_k + \nu - k^2), \tag{35}$$

and the current from this unscattered contribution is

$$j_0 = \int 2ep\, f(p)\, \frac{dp}{2\pi} = eA\int_0^{\infty} dk\left(TM^2\,\frac{\delta l}{\delta + l}\right)\delta(\epsilon_k + \nu - k^2). \tag{36}$$

Apart from the factor in the large parentheses, the integral in (36) is the joint density of states. Therefore the rate of emission of nonscattered electrons is essentially proportional to the product of the squared matrix element, the joint density of states, the transmission probability of the surface, and an effective depth which is the harmonic mean of the skin depth and the mean free path.

III. VERTEX CORRECTION

The diagrammatic expansion for $\langle GG\rangle_{\mathrm{av}}$ in terms of g is well known,[9] and for $1/\tau \ll E$, it is given exactly by the sum of diagrams shown in Fig. 1(b). Physically, these diagrams represent contributions to the photocurrent by electrons which have been scattered zero, one, two, or more times, respectively, before escaping.

From Fig. 1(b), then, it is clear that we must solve the integral equation

$$\begin{aligned}\langle G(x_1, x_1'; E+i\eta)\, &G(x_2', x_2; E-i\eta)\rangle_{\mathrm{av}}\\ &= g(x_1, x_1'; E+i\eta)\, g(x_2', x_2; E-i\eta)\\ &\quad + \int n(r)dr \int d\bar{x}_1 \int d\bar{x}_2 \int d\tilde{x}_1 \int d\tilde{x}_2\\ &= g(x_1, \bar{x}_1; E+i\eta)\, g(\bar{x}_2, x_2; E-i\eta)\\ &\quad \times t_r(\bar{x}_1; \tilde{x}_1; E+i\eta)\, t_r(\tilde{x}_2, \bar{x}_2; E-i\eta)\\ &\quad \times \langle G(\tilde{x}_1, x_1'; E+i\eta)\, G(x_2', \tilde{x}_2; E-i\eta)\rangle_{\mathrm{av}}\,. \end{aligned} \tag{37}$$

We now make the local assumption for t made earlier; that is,

$$t_r(x, x') = t\delta(r-x)\delta(x-x')\,.$$

Defining

$$F(x, x') = \langle G(x, x'; E+i\eta)\, G(x', x; E-i\eta)\rangle_{\mathrm{av}} \tag{38}$$

and

$$F_0(x, x') = g(x, x', E+i\eta) g(x, x', E-i\eta)\,, \tag{39}$$

we obtain

$$F(x, x') = F_0(x, x') + \alpha \int_{-\infty}^{0} d\bar{x}\, F_0(x, \bar{x}) F(\bar{x}, x')\,, \tag{40}$$

where

$$\alpha = n|t|^2 = 2E/l\,. \tag{41}$$

The function $F(x, x')$ is clearly all that is needed to obtain the full four-argument function $\langle GG\rangle_{\mathrm{av}}$.

The function F_0, obtained essentially by squaring (30), has three terms for x and x' less than zero; all three terms are exponentially small for x and x' widely separated from each other and the surface. The cross term, however, has in addition a rapid sinusoidal variation which arises from the phase memory of an electron reflecting off the surface; that is, the reflected wave interferes with the incident wave. This phase memory would not occur, and the sinusoidal term in F_0 would average to zero, if the position of the surface for each subsequent reflection were random on the scale of the photoelectron's de Broglie wavelength, which is rather small if the electron is to escape ultimately. Since the presence of the sinusoidal term in F_0 makes (40) more difficult to solve, and because a physical surface probably is diffuse, we neglect this interference term, taking

$$F_0(x, x') = (1/4E)(Re^{(x+x')/l} + e^{-|x-x'|/l}) \quad \text{for } x < 0 \text{ and } x' < 0 \; . \tag{42}$$

In fact, it would be inconsistent to do otherwise in view of our earlier approximation of constant τ in Eq. (24).

Note that F_0, as well as any finite-order iteration of (40), is a sum of decaying exponentials. However, the exact solution is qualitatively different:

$$\begin{aligned} F(x, x') &= \frac{1}{2E}\left(\frac{1+R}{1-R} - \frac{x}{l}\right) \quad \text{for } 0 > x > x' \\ &= \frac{1}{2E}\left(\frac{1+R}{1-R} - \frac{x'}{l}\right) \quad \text{for } x < x' < 0. \end{aligned} \tag{43}$$

The reason for the difference relates to the failure of any finite iteration of (40) to satisfy the Baym[10] self-consistency criteria; that is, any nth-order perturbation theoretic solution fails to conserve particles because it essentially assumes that any electron disappears after it is scattered n times. Thus the scattering does not prevent electrons from reaching the surface from long distances, and the evanescence of the vertex function at these distances is the fiction of a poor approximation.

The contribution to $f(p)$ by those electrons that have scattered at least once is [according to Eq. (19) and Fig. 1(b)]

$$\begin{aligned} \delta f(p) = {} & (2/\pi)|A|^2 \int_0^\infty dR\, |M|^2 \int_{-\infty}^\infty dx\, e^{-px} \\ & \times \left\{ \int_{-\infty}^0 d\bar{x} \left[\int_{-\infty}^0 dx'\, e^{x/2\delta} \sin(kx' + \alpha) g(x', \bar{x}) \right] \right\} \\ & \times (2E/l) \langle G(\bar{x}, r - \tfrac{1}{2}x;\; E + i\eta) G(r + \tfrac{1}{2}x;\; E - i\eta) \rangle_{\text{av}} \, , \end{aligned} \tag{44}$$

where $E = \epsilon_k + \nu$. The quantity

$$\langle G(\bar{x}, r - \tfrac{1}{2}x) G(r + \tfrac{1}{2}x, x) \rangle_{\text{av}} \quad \text{for } \bar{x} < 0, \; r \pm \tfrac{1}{2}x > 0$$

may be simply evaluated:

$$\begin{aligned} & \langle G(\bar{x}; r - \tfrac{1}{2}x;\; E + i\eta) G(r + \tfrac{1}{2}x, \bar{x};\; E - i\eta) \rangle_{\text{av}} \\ & \quad = g(\bar{x};\; r - \tfrac{1}{2}x;\; E + i\eta) g(r + \tfrac{1}{2}x;\; \bar{x};\; E - i\eta) \\ & \qquad + (2E/l) \int_{-\infty}^0 d\bar{x}'\, F(\bar{x}, \bar{x}') g(\bar{x}' r - \tfrac{1}{2}x;\; E + i\eta) \\ & \qquad \times g(\bar{x}', r + \tfrac{1}{2}x;\; E - i\eta) \; . \end{aligned} \tag{45}$$

Using (30) and (43), we obtain

$$\langle G(\bar{x}; r - \tfrac{1}{2}x;\; E + i\eta) G(r + \tfrac{1}{2}\bar{x};\; E - i\eta) \rangle_{\text{av}} = (2p_1 p_2)^{-1} e^{-p_2 x} \tag{46}$$

independent of $\bar{x}$ and r (provided that $\bar{x} < 0$, $r \pm \frac{1}{2}x > 0$). Thus, the only further quantity needed is that in the curly brackets in (44). We cannot use (32) for this because now x' and $\bar{x}$ are both negative, so that g is now more complicated and has more analytic segments. In fact there are now eight terms instead of two in the analog of (32) and hence 64 terms in the curly brackets. As before, these simplify considerably in our case where δ^{-1} and l^{-1} are much less than the wave vector of the photoelectron. In this case the curly brackets in (44) are simply equal to

$$\frac{l}{16E}\left(2\delta - \frac{\delta l}{\delta + 1} T\right) 2\pi\delta(p_1 - k) \; . \tag{47}$$

Therefore (44) becomes

$$\delta f(p) = \pi A^2 \int_0^\infty dk\, \frac{\delta(p_2 - p)}{p} M^2 \times \left(2\delta - \frac{\delta l}{\delta + l} T\right) \delta(\epsilon_k + \nu - k^2) \; . \tag{48}$$

Therefore the whole asymptotic distribution function $f(p) = f_0(p) + \delta f(p)$ is

$$f(p) = \pi A^2 \int_0^\infty dk\, \frac{\delta(p_2 - p)}{p} M^2 (2\delta) \delta(\epsilon_k + \nu - k^2) \, , \tag{49}$$

and the total photocurrent

$$j = eA^2 \int_0^\infty dk\, M^2 (2\delta) \delta(\epsilon_k + \nu - k^2) \; . \tag{50}$$

Note that this is completely independent of the mean free path l and of the transmission coefficient of the surface, T. We may also calculate the fraction of photoelectrons that escape without scattering

$$j_0 / j = \tfrac{1}{2} T\, l/(l + \delta) \; . \tag{51}$$

We now show that Eq. (40) for the vertex function is the same as the rate equation for photoelectric emission written down by Kane by intuitive considerations [Eq. (5) of his paper]. To do this we let x' be outside the sample, while x is inside, so that $F(x, x')$ is independent of x'. For these values of x and x', $F_0(x, x')$ is given by

$$F_0(x, x') = (1/4p_1 p_2) T e^{x/l} \, , \tag{52}$$

where we have used (26), (29), and (39), plus the usual approximation that l is much longer than the de Broglie wavelength. Defining

$$p_0(x) \equiv 2p_1 p_2 F_0(x, x') = \tfrac{1}{2} T e^{x/l} \tag{53}$$

and

$$q(x) = 2p_1 p_2 F(x, x') \, , \tag{54}$$

where $x' > 0$, and substituting (42), (53), and (54) into (40) gives

$$q(x)=p_0(x)+\frac{1}{2l}\int_{-\infty}^{0} dx'\left|Re^{(x+x')/l}+e^{-|x-x'|/l}\right|q(x') . \tag{55}$$

This is the same as Kane's Eq. (5), except that we have not added a nonconserving scattering mechanism as he has. This could, of course, easily been done in an *ad hoc* manner by letting the coefficient in the exponents in (55) be greater than l^{-1}.

IV. CONCLUSIONS

An important accomplishment of this work is to derive rigorously from first principles Kane's rate equations for photoelectric emission and, hence, his results; this is a derivation of the photoelectric rate equations in the same sense that the work of Langer and others constitutes a derivation of the Boltzmann equation for impurity scattering in the bulk. The derivation makes clear that although the rate equation is not exact (just as the Boltzmann equation is not exact) even for this idealized model, it is nevertheless a very good approximation for most reasonable values of the parameters.

Let me now list several other conclusions, which although implicit or explicit in Kane's work, have not, I believe, been fully appreciated within the context of the first-principles type of calculation fashionable today. The first is that the true vertex function for scattering is qualitatively different from any perturbation theoretic approximation to it, no matter how weak the scattering. Thus an infinite order of scattering must always be considered. Of course, the conclusion that the vertex function no longer decays exponentially at all, depends on the (inexact) assumption of elastic scattering; in a more realistic case, the true vertex function would still decay, but at a much slower rate than perturbation theoretic approximations to it. Said another way, photoelectrons emerging from the surface can originate from points much deeper in the bulk than the mean free path. A final point is that even in the limit of infinitesimally weak scattering, the photocurrent is not given accurately by neglecting scattering from the beginning, that is, the order of the limits is important. This may be seen most clearly by noting that as the mean free path becomes infinite, the ratio (51) does *not* approach unity, but rather $\frac{1}{2}T$. The physical reasons for this is clear and have been discussed before,[6] but have not, I believe, been adequately appreciated by those doing first-principles calculation. Note that the effect is especially pronounced near threshold where T is small, so that the scattered electrons would dominate the photocurrent, and thus would obscure the angular dependence of the intensity of unscattered electrons.

These general conclusions probably do not depend on the details of most of the various simplifying assumptions of our model, such as the one dimensionality and the locality of the self-energy, although the details of the energy distributions surely do. Said another way, it is our guess that (51) is more general than its derivation. The most important effect in real systems not included here is inelastic scattering. This will, of course, completely change the momentum decomposition of the emitted photoelectrons, that is, the scattered ones no longer have the joint density-of-states–type relation. However, for electrons of energy sufficiently high that the fractional energy loss per collision is small, then formula (51) should still be qualitatively valid, even though the momentum decomposition in (48) is clearly wrong. Except for the surface effect, the three-dimensional version of (35) will be right in any case (when properly calculated with the true band structure and matrix elements) and (51) can be used to estimate what fraction of the photoelectrons are given by (35).

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