Theory of the Surface Photoelectric Effect for One and Two Photons*

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The theory of the surface photoelectric effect for the absorption of one and two photons is discussed systematically using Green's functions. The asymptotic form of Green's function leads naturally to the incoming wave solution used previously by Makinson. By exploiting a commutation relation between the operators of momentum and Green's function, one can express the amplitude of the electron outgoing wave in a series which involves explicitly the force and the potential acting on the electron. In the Wentzel, Kramers, Brillouin, and Jeffreys (WKBJ) approximation, valid for a slowly varying potential, the leading term of the series gives the major contribution. In the other extreme, where the potential varies rapidly in an electron wavelength all terms can be approximately evaluated. In particular, for the square-well potential the results are immediate. Other simple examples are given to illustrate the method. A discussion of the second-order photocurrent is given and our results are compared with earlier work. Finally, the equivalence of two models used in surface problems is discussed. It is shown that the finite plate model reduces to the semi-infinite model if one takes the average of the wave function, and not its square, as the plate thickness becomes infinitely large.

I. INTRODUCTION

THIS paper deals with a systematic theoretical study of the surface photoelectric effect in solids, for one and two photons. In the surface photoelectric effect an electron absorbs photons as a result of the variation in the potential which the electron sees near the surface of the metal. This mechanism is to be distinguished from the volume photoelectric effect which takes place *directly* by interband transitions, or *indirectly* when a third system such as a phonon or an impurity participates in the interaction of an electron and a photon.

The model we shall analyze is rather simple and idealized. We consider an electron gas which is free, except for a general surface potential, which does not depend on the electron energy. The pioneering work of Bardeen[1] on the nature of the surface potential in metals indicates that this potential is a function of the electron wave number k, and some theories of the photoelectric effect[2,3] have made use of this result. However, this early work of Bardeen ought to be reconsidered in the light of recent work on the theory of the electron gas. The work of Bohm and Pines,[4] and others, suggest that the exchange and correlation effects are reduced as a result of the screening of the Coulomb interaction between the electrons. This would tend to justify the approximation that each electron sees the same potential. The radiation field will be quantized, and the interaction of electrons with the incident wave alone will be considered.[5]

In Sec. II we shall discuss our approach which is based on the methods of Green's functions and the formal theory of scattering.[6–8] This approach is general and systematic. It allows one to single out the terms which are relevant to the calculation of the photoelectric current. The amplitude of the photoelectron wave, far outside the metal, follows directly from the asymptotic form of Green's function. The "incoming wave" used by Makinson[2] is thus obtained in a natural way. We shall, however, point out that the factorization of the transmission coefficient by Makinson is somewhat arbitrary. We shall find occasion to give a new and simple derivation of the famous "incoming wave" solution which is used in computing scattering cross sections.[9,10] This derivation will hold in any number of dimensions.

The one and two photon matrix elements are cast in a convenient form by exploiting a commutation relation between Green's function and momentum. The potential and the force acting on the electron occur explicitly in the matrix elements. For a slowly varying potential, the calculation of the first- and second-order photoelectric current reduce, approximately, to the evaluation of only single integrals. For a rapidly varying potential, such as a square well, the results are immediate.

In Sec. III we calculate the photoelectric effect using simple surface potentials, namely, a linear and a square-well potential. We shall see how the results of Smith[11] on the second-order photoelectric effect, which happen to contain some unfortunate errors, can be

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[1] J. Bardeen, Phys. Rev. **49**, 653 (1936).

[2] R. E. B. Makinson, Phys. Rev. **75**, 1908 (1949).

[3] M. J. Buckingham, Phys. Rev. **80**, 704 (1950).

[4] See D. Pines in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 367.

[5] A rigorous theory of reflection and refraction is far from complete at the present time. The work of L. I. Schiff and L. H. Thomas, Phys. Rev. **47**, 860 (1935); and R. E. B. Makinson, Proc. Roy. Soc. (London) **A162**, 367 (1937), might offer a good starting point.

[6] B. A. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950).

[7] M. Gell-Mann and M. L. Goldberger, Phys. Rev. **91**, 398 (1953).

[8] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic Press Inc., New York, 1957), Sec. 9.

[9] See G. Breit and H. A. Bethe, Phys. Rev. **93**, 888 (1954).

[10] I. Adawi, Am. J. Phys. **32**, 211 (1964).

[11] R. L. Smith, Phys. Rev. **128**, 2225 (1962).

correctly derived from our formulas in a few steps. It is also possible to obtain useful approximations without resort to numerical integrations.

We shall discuss two models which have been used in the study of the photoelectric effect,[12–14] and other surface problems.[15] Fröhlich,[12] and Sommerfeld and Bethe[13] have used a finite plate model which has two surfaces. Mitchell,[14] and latter workers, on the other hand, have used the semi-infinite model which has only one surface. The aim of the discussion, aside from illustrating our methods, is to bring out clearly that the two models, *as used*, lead to different results, even when the width of the finite plate approaches infinity. Indeed, Mitchell might have realized the difficulty and the need for reconciling the results of the two models. However, he made no effort to settle the question, and since then the problem seems to have been forgotten. We shall resolve the difficulty in Sec. IV by describing a limiting procedure by which one can pass from a model with two surfaces to the semi-infinite model with one surface.

There have been so far no experimental reports on two-photon photoelectric effect. It is hoped that future experiments with optical masers would succeed in disentangling this effect from other possible effects, as our understanding of the various interaction mechanisms improves. It is of interest to observe that Makinson and Buckingham[16] have anticipated a second-order surface photoelectric effect long before optical masers were known. Their work forms an obvious extension to Makinson's[2] earlier paper, and their method, as they state, applies only when the first-order effect is absent. In contrast our method holds regardless of the absence or presence of the first-order effect, and our point of view is entirely different.

II. DERIVATION

A. General Considerations

Take the x axis normal to the surface of the solid, and let the static potential V, in which the electron moves, vary only in the x direction. Restricting the discussion to a single electron band, the electron motion in the y and z directions is separable and can be described by the wave function $\exp i(k_y y+k_z z)$ normalized to one particle per unit surface area and satisfying cyclic boundary conditions. The unperturbed Hamiltonian H_0 of the problem consists of the electron Hamiltonian H_e describing the electron motion in the potential $V(x)$, and the free radiation Hamiltonian H_r:

$$H_0=H_e+H_r=\frac{1}{2m}p_x^2+V(x)+\sum_\beta a_\beta^\dagger a_\beta\hbar\omega_\beta, \quad (2.1)$$

where $a_\beta^\dagger$ and a_β are the creation and annihilation operators for the radiation oscillator β of angular frequency ω_β, and p_x and m are the electron momentum and mass.

In the nonrelativistic approximation the electron-photon interaction H_1 consists of a linear and a quadratic term in the vector potential[17] **A**. To the extent that we neglect retardation and restrict the calculation to the absorption of one and two photons, the A^2 term is of no interest. The only term of interest is given by

$$H_1=\sum_\beta \frac{e\hbar}{im}\left(\frac{2\pi\hbar}{\omega_\beta}\right)^{1/2}(\mathbf{e}_\beta\cdot\hat{x})a_\beta\frac{\partial}{\partial x}\equiv\sum_\beta\gamma_\beta a_\beta D, \quad (2.2)$$

where e is the electron charge, $\mathbf{e}_\beta$ is the polarization unit vector parallel to $\mathbf{A}_\beta$, and $\hat{x}$ is a unit vector in the x direction. The parameter γ_β is defined by Eq. (2.2) in which D is used, for convenience, instead of $\partial/\partial x$. The radiation field has been quantized in a unit volume.

We shall now use the steady-state method of scattering theory[6–8] which is, of course, equivalent to the time proportional transitions method. In the initial state ψ_0, let the electron be in state ϕ_0 with $H_e\phi_0=E_0\phi_0$, and the occupation numbers $n_{\beta'}$ of the radiation oscillators are all zero except n_β. The initial state is conveniently written as $\psi_0=|n_\beta,\phi_0\rangle$ and the initial energy $\mathcal{E}_0=E_0+n_\beta\hbar\omega_\beta$. The final state ψ^+, for outgoing waves, is a solution of the scattering equation:

$$\psi^+=|n_\beta,\phi_0\rangle+\frac{1}{\mathcal{E}_0-H_0+i\epsilon}H_1\psi^+. \quad (2.3)$$

Let

$$\begin{aligned}&\psi^+=\psi_0+\psi_1+\psi_2,\\ &\psi_1=\gamma_\beta n_\beta^{1/2}|n_\beta-1,\phi_1\rangle,\\ &\psi_2=\gamma_\beta^2[n_\beta(n_\beta-1)]^{1/2}|n_\beta-2,\phi_2\rangle.\end{aligned} \quad (2.4)$$

It follows that the first- and second-order electron states are given by

$$\phi_1=G_1D\phi_0, \quad (2.5)$$

$$\phi_2=G_2DG_1D\phi_0, \quad (2.6)$$

where the one electron Green's function[18] G_r is defined for $r=1, 2$, by

$$\begin{aligned}&G_r=(E_r-H_e+i\epsilon)^{-1},\\ &E_r=E_0+r\hbar\omega_\beta.\end{aligned} \quad (2.7)$$

[12] H. Fröhlich, Ann. Physik **7**, 103 (1930).

[13] A. Sommerfeld and H. A. Bethe, in *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer Verlag, Berlin, 1933), 2nd ed., Vol. 24, p. 467.

[14] K. Mitchell, Proc. Roy. Soc. (London) **A146**, 442 (1934).

[15] The same two models were used in the study of the surface effect in secondary emission from metals. E. M. Baroody, Phys. Rev. **92**, 843 (1953) uses the semi-infinite model; while W. Brauer and W. Klose, Ann. Physik **19**, 116 (1956), use the finite plate model. We shall treat this problem in a forthcoming paper [I. Adawi, Phys. Rev. (to be published)].

[16] R. E. B. Makinson and M. J. Buckingham, Proc. Phys. Soc. (London) **A64**, 135 (1951). This paper was brought to our attention after the major portions of our paper were completed; we had however anticipated it.

[17] See, e.g., W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, New York, 1954), 3rd ed., Sec. 13 and 14.

[18] It is customary to write G_r^+ instead of G_r for outgoing waves. Since we shall not discuss here other types of Green's function the + sign will be dropped.

The energy scale is such that an electron at rest at $x=\infty$ has zero energy, or alternatively $V(\infty)=0$.

In the photoelectric effect one is interested in the amplitude of the outgoing electron wave. This is determined in Eqs. (2.5) and (2.6) by the asymptotic behavior of G_1 and G_2 in the position representation.

B. Asymptotic Behavior of $G(x,y)$

The one-dimensional case will be treated first as a special case of Green's function for the wave equation in any number of dimensions. This slight diversion is made to give a rigorous but not laborious derivation of the famous "incoming wave" solution.[9] Let $\mu=2m/\hbar^2$, $G=\mu g$, $U=\mu V$, $q^2=\mu E$, where E is the wave energy, and let Δ be the Laplacian in n dimensions. From the operational identity,

$$g=\frac{1}{q^2+\Delta-U+i\epsilon}\equiv\frac{1}{q^2+\Delta+i\epsilon}\left(\frac{1}{g}+U\right)g$$
$$=g_0+g_0Ug\,,$$

we obtain

$$g(\mathbf{x},\mathbf{y})=g_0(\mathbf{x},\mathbf{y})+\int g_0(\mathbf{x},\mathbf{z})U(\mathbf{z})g(\mathbf{z},\mathbf{y})d^nz\,, \quad (2.8)$$

where g_0 is the free space ($U=0$) Green's function. Since,[19]

$$g_0(\mathbf{x},\mathbf{y})=(4i)^{-1}(q/(2\pi|\mathbf{x}-\mathbf{y}|))^{(n-2)/2}\times H_{(n/2)-1}{}^{(1)}(q|\mathbf{x}-\mathbf{y}|)\,, \quad (2.9)$$

we have for large x and finite y,

$$g_0(\mathbf{x},\mathbf{y})\sim(2iq)^{-1}(-iq/2\pi x)^{(n-1)/2}e^{iqx}e^{-i\mathbf{q}\cdot\mathbf{y}}\,, \quad (2.10)$$

where $\mathbf{q}$ is parallel to $\mathbf{x}$. Use (2.10) in (2.8) and substitute the symmetry relation $g(\mathbf{y},\mathbf{z})=g(\mathbf{z},\mathbf{y})$ to obtain the asymptotic formula,

$$g(\mathbf{x},\mathbf{y})\sim(2iq)^{-1}(-iq/2\pi x)^{(n-1)/2}e^{iqx}v(\mathbf{y})\,, \quad (2.11)$$

$$v(\mathbf{y})=e^{-i\mathbf{q}\cdot\mathbf{y}}+\int g(\mathbf{y},\mathbf{z})U(\mathbf{z})e^{-i\mathbf{q}\cdot\mathbf{z}}d^nz\,. \quad (2.12)$$

v, as defined by (2.12), represents an incident plane wave moving in $-\mathbf{x}$ direction plus an *outgoing* scattered wave, and satisfies the wave equation $(q^2+\Delta-U)v=0$. Alternatively, v^* represents a solution of the wave equation corresponding to an incident plane wave moving in the direction of observation $\mathbf{x}$ and a scattered *incoming* wave.

For a general perturbation H', the perturbed problem requires the solution of an equation of the type (2.5), namely, $\phi=GH'\phi_0=\mu gH'\phi_0$. The amplitude $\mathfrak{A}$ of the outgoing electron wave follows from substituting (2.11) into this equation and we have

$$\phi(\mathbf{x})\sim\mathfrak{A}e^{iqx}\equiv(-im/\hbar^2q)(-iq/2\pi x)^{(n-1)/2}\times\langle v^*|H'|\phi_0\rangle e^{iqx}. \quad (2.13a)$$

In the transition matrix element, $\langle v^*|H'|\phi_0\rangle$, the potential V is treated exactly while H' is treated to first order. The simplest version of the Born approximation neglects the integral term in (2.12) corresponding to the scattered wave and thus replaces v by a plane wave. The particle current dI in a solid angle element $d\Omega_n$ at $\mathbf{x}$ is given by the current density $(\hbar q/m)|\mathfrak{A}|^2$ multiplied by the area element $x^{n-1}d\Omega_n$, namely,

$$dI=(m/\hbar^3q)(q/2\pi)^{n-1}d\Omega_n|\langle v^*|H'|\phi_0\rangle|^2. \quad (2.13b)$$

This is precisely what one would obtain from the time-dependent approach[7] for the transition rate to the plane-wave states $e^{i\mathbf{q}\cdot\mathbf{r}}$, where $\mathbf{q}$ lies in the solid angle element $d\Omega_n$ centered at $\mathbf{x}$, and in the energy shell of thickness δE centered at E. The factor multiplying $|\langle v^*|H'|\phi_0\rangle|^2$ in (2.13b) is simply $(2\pi/\hbar)\rho(E)$. Since the final states have been normalized to one per unit volume, the density of final states $\rho(E)$ is the volume in q space divided by $(2\pi)^n\delta E$, namely,

$$\rho(E)=d\Omega_nq^{n-1}(dq/dE)(2\pi)^{-n}=d\Omega_n(q/2\pi)^{n-1}(m/2\pi\hbar^2q)\,.$$

For one dimension (2.11) gives the asymptotic formula,

$$G_r(x,y)\sim(\mu/2iq_r)\exp(iq_rx)v_r(y)\,, \quad (2.14)$$

whose application to Eqs. (2.4) and (2.5) yields the first-order photocurrent element dI_1.

$$dI_1=e(m/\hbar^3q_1)|\gamma_\beta|^2n_\beta|M_1|^2 \quad (2.15a)$$

$$M_1=\langle v_1^*|D|\phi_0\rangle. \quad (2.15b)$$

Equations (2.15a,b) are a special case of Eq. (2.13b) in which we set $n=1$, $d\Omega_1=1$ (the total solid angle in one dimension being 2, one for each direction), and $H'=\gamma_\beta n_\beta{}^{1/2}D$.

The second-order photocurrent element dI_2 is similarly obtained by applying (2.14) to (2.4) and (2.6). We notice that $G_1D\phi_0$ in (2.6) plays the role of ϕ_0 in (2.5). Expanding G_1 in terms of the eigenfunctions ϕ_j of H_e, namely, $G_1(x,y)=\sum_j\phi_j(x)\phi_j^*(y)[E_1-E_j+i\epsilon]^{-1}$, where $H_e\phi_j=E_j\phi_j$, we obtain

$$dI_2=e(m/\hbar^3q_2)\gamma_\beta{}^4n_\beta(n_\beta-1)|M_2|^2, \quad (2.16a)$$

$$M_2=\sum_j\langle v_2^*|D|\phi_j\rangle\langle\phi_j|D|\phi_0\rangle(E_1-E_j+i\epsilon)^{-1}\equiv\langle v_2^*|DG_1D|\phi_0\rangle. \quad (2.16b)$$

The total current element[20] dI is the sum of dI_1 and dI_2. dI_r is zero if E_r is negative.

[19] Equation (2.9) can be derived by remembering that $\Delta|\mathbf{x}|^{n-2}=-4\pi^{n/2}\delta^n(\mathbf{x})/\Gamma(\frac{1}{2}n-1)$ for $n\neq2$ and $\Delta\ln x=2\pi$ for $n=2$, and examining the behavior of Hankel's function for small values of the argument. See, e.g., E. Janke and F. Emde, *Tables of Functions*, (Dover Publications, Inc., New York, 1945), 4th ed., p. 133.

[20] In calculating the current element we use the usual formula,

$$dI=(e\hbar/2mi)\langle\psi^*(\partial\psi/\partial x)-\psi(\partial\psi^*/\partial x)\rangle_{\mathrm{av}}-(e^2/mc)\langle\psi^*\hat{x}\cdot\mathbf{A}(t)\psi\rangle_{\mathrm{av}},$$

where the average signs imply an integration over the radiation coordinates. Here, ψ is used for Ψ^+ of (2.4) and the vector potential is expressed in terms of the creation and annihilation operators in

We shall now exploit the simplicity of the one-dimensional model itself. For positive energy E the wave equation has in addition to the solution $v(x)$ another independent solution $u(x)$ where u corresponds to a wave incident from the left, reflected, and transmitted to the right. The solutions u and v are best described by their asymptotic behavior using the scattering matrix S. Let the propagation constants of the wave at $x=\infty$ and $x=-\infty$ be q and k, respectively, i.e., $q^2=\mu E$ and $k^2=\mu[E-V(-\infty)]$. For the finite plate potential model $q=k$, since $V(-\infty)=0$, but $q\neq k$ for the semi-infinite potential model for which $V(-\infty)$ approaches a negative constant $-V_0$. The amplitudes of the scattered waves $(\alpha_2 e^{-ikx},\alpha_1 e^{iqx})$ are related to those of the incident waves $(a_2 e^{ikx},a_1 e^{-iqx})$ by the matrix equation:

$$\begin{pmatrix}\alpha_1\\ \alpha_2\end{pmatrix}=S\begin{pmatrix}a_1\\ a_2\end{pmatrix}. \tag{2.17}$$

With this notation, in which the *comma* separates the behavior of the function for $x=-\infty$ and ∞, we write the asymptotic equations:

$$u(x)\sim(e^{ikx}+S_{22}e^{-ikx},\ S_{12}e^{iqx}), \tag{2.18}$$

$$v(x)\sim(S_{21}e^{-ikx},\ S_{11}e^{iqx}+e^{-iqx}). \tag{2.19}$$

From these definitions, the Wronskian $W(v,u)=2iqS_{12}$ and Green's function can be written down

$$G(x,y)=(\mu/2iqS_{12})[v(x)u(y) \quad \text{and} \quad v(y)u(x)] \quad \text{for } x<y \text{ and } x>y. \tag{2.20}$$

Eqs. (2.18)–(2.20) give immediately (2.14).

The procedure followed by Makinson[2] amounts to writing our function v as $S_{21}\chi$. Using χ instead of v in (2.15) and (2.16) Makinson[2] concludes that the photoelectric current is proportional to the transmission coefficient of the potential since $|S_{21}|^2(k/q)$ is the transmission coefficient. This reasoning is open to question, for equally well we could define a new function $\bar{\chi}$ by writing $v=S_{11}\bar{\chi}$ where

$$\bar{\chi}\sim((S_{21}/S_{11})e^{-ikx},\ e^{iqx}+(1/S_{11})e^{-iqx}).$$

Using $\bar{\chi}$ instead of v we would conclude that the photocurrent is proportional to $|S_{11}|^2$ which is the reflection coefficient of the potential. The correct conclusion seems to be that the characteristics of the potential enter implicitly the matrix elements M_1 and M_2 which determine the photocurrent, but it hardly serves any useful purpose to factor out a transmission or a reflection coefficient in the manner just described.

The functions u and v are orthogonal and can be properly normalized. They form with the bound states a complete set of functions. It is such a set which is implied by the summation in (2.16b) over the intermediate states ϕ_j. This set of functions is more suitable to use in the variation of the constants method than the set used by Mitchell.[14] The details are given in the Appendix.

C. Results and Discussion

We shall now cast the functions ϕ_1 and ϕ_2 in a convenient form using the following commutation relation in (2.5) and (2.6):

$$\begin{aligned}GD&\equiv GD[E-H_e+i\epsilon]G\\ &=G[-V'+(E-H_e+i\epsilon)D]G\\ &=DG-GV'G,\end{aligned} \tag{2.21}$$

where $-V'$ is the force on the electron.[21] Observing that,

$$G_r\phi_0=(r\hbar\omega_\beta)^{-1}\phi_0, \tag{2.22}$$

$$G_1G_2=(\hbar\omega_\beta)^{-1}(G_1-G_2), \tag{2.23}$$

we obtain the basic equations:

$$(\hbar\omega_\beta)\phi_1=\phi_0'-G_1V'\phi_0, \tag{2.24}$$

$$(\hbar\omega_\beta)\phi_2=G_2\phi_0''+f_2, \tag{2.25}$$

$$f_2=-G_2DG_1V'\phi_0, \tag{2.26}$$

$$(\hbar\omega_\beta)f_2=-DG_1V'\phi_0+DG_2V'\phi_0+G_2V'(G_1-G_2)V'\phi_0. \tag{2.27}$$

To illustrate this compact notation we give an example:

$$DG_1V'\phi_0\equiv(\partial/\partial x)\int G_1(x,y)V'(y)\phi_0(y)dy. \tag{2.28}$$

Equations (2.24)–(2.27) will now be used to derive and discuss more convenient expressions for the matrix elements M_1 and M_2 than those given by (2.15) and (2.16). The procedure is the same as before; we use (2.14) to examine the asymptotic behavior of ϕ_r, $r=1$, 2, and set the amplitude of the outgoing wave $\exp(iq_rx)$ equal to $(\mu/2iq_r)M_r$. In (2.24) the term $\phi_0'\sim0$ since ϕ_0 is a bound state, and the term $\phi_1\sim-G_1V'\phi_0/(\hbar\omega_\beta)$ yields

$$M_1=-(\hbar\omega_\beta)^{-1}\langle v_1^*|V'|\phi_0\rangle. \tag{2.29}$$

The form (2.29) for M_1 might be more convenient to use than (2.15b), since the range of integration is limited only to the region where the potential is variable. The three dimensional version of (2.29) is well known although less practical than the dipole matrix element.[22] It is possible to derive (2.29) from (2.15b) by considering the matrix element $\langle v_1^*|[D,H_e]|\phi_0\rangle$ and using the commutation relation $[D,H_e]=V'$.

If E_1 is negative M_1 is zero and $G_1V'\phi_0\sim0$ and $DG_1V'\phi_0\sim0$ in (2.27). If E_1 is positive $G_1V'\phi_0$ is a free state; however, for the integral $G_2DG_1V'\phi_0$ which

the Heisenberg representation. If both E_1 and E_2 are positive, we have in addition to the terms dI_1 and dI_2 an interference term, due to $\mathbf{A}$, between ψ_1 and ψ_2 which oscillates with the radiation frequency and has an average zero. However, in the final state, $\psi_1+\psi_2$, the photoelectron and the photons fly apart and are spatially separated. The vector potential $\mathbf{A}$ at the position of the electron is then small, and the interference term must be negligible.

[21] The relation (2.21) can also be derived by operating on both sides of the differential equation, $(E-H_e)G(x,y)=\delta(x-y)$, by $(\partial/\partial x+\partial/\partial y)$ and carrying out some elementary manipulations.

[22] See Ref. 8, Sec. 59.

defines f_2 in (2.26) to exist, a convergence factor (cutoff) must be applied to the function $G_1V'\phi_0$. With this in mind the function $DG_1V'\phi_0$ is to be assigned the asymptotic value zero in (2.27). The remaining terms in (2.25) and (2.27) give asymptotically an outgoing wave of the form $\exp(iq_2x)$ which is what we would expect from energy conservation, since the physical process corresponds to an electron absorbing two photons. The matrix element M_2, for positive E_2, consists of the contributions of the three terms which contain $G_2\phi_0''$, $DG_2V'\phi_0$, and $G_2V'(G_1-G_2)V'\phi_0$, and these we shall denote by M_2^1, M_2^2, and M_2^3, respectively. By definition,

$$M_2=M_2^1+M_2^2+M_2^3. \tag{2.30}$$

With the aid of (2.14) we find that

$$M_2^1=(\hbar\omega_\beta)^{-1}\langle v_2^*|D^2|\phi_0\rangle, \tag{2.31}$$

which can be written as

$$M_2^1=\mu(\hbar\omega_\beta)^{-1}\langle v_2^*|V|\phi_0\rangle \tag{2.32}$$

using Schrödinger's equation and the orthogonality of v_2 and ϕ_0. Similarly,

$$M_2^2=iq_2(\hbar\omega_\beta)^{-2}\langle v_2^*|V'|\phi_0\rangle, \tag{2.33}$$

$$M_2^3=(\hbar\omega_\beta)^{-1}\sum_j\langle v_2^*|V'|\phi_j\rangle\langle\phi_j|V'|\phi_0\rangle \times[(E_1-E_j+i\epsilon)(E_2-E_j+i\epsilon)]^{-1}. \tag{2.34}$$

M_2 as given by (2.30)–(2.34) is, of course, equivalent to (2.16b), but it is not possible to derive Eqs. (2.30)–(2.34) from (2.16b) alone (without introducing G_2) since (2.16b) does not contain G_2 in full and we have no longer access to the commutation relation of G_2 and D. If in (2.16b) we use the commutation relation of G_1 and D twice, remembering that $\langle v_2^*|G_1=-(\hbar\omega_\beta)^{-1}\langle v_2^*|$, we see that (2.16b) gives exactly the same thing as (2.30)–(2.34) provided that

$$\langle v_2^*|D|V'\phi_0\rangle=iq_2\langle v_2^*|V'|\phi_0\rangle-\langle v_2^*|V'G_2V'|\phi_0\rangle. \tag{2.35}$$

(2.35) is an identity which follows from the asymptotic form of the commutation relation (2.21) when $G=G_2$.

For situations of practical interest V, $\hbar\omega_\beta$ and E_2 are of the same order of magnitude, namely, a few electron volts, and we shall not distinguish between these energies in the following estimates. Assuming $V'\sim O(\kappa V)$, where O is an order of magnitude symbol, we see that $M_2^1:M_2^2\sim 1:\kappa/q_2$. The matrix element M_2^3 can be given the estimate,

$$M_2^3\sim O[(\hbar\omega_\beta)^{-3}\langle v_2^*|(V')^2|\phi_0\rangle], \tag{2.36}$$

and consequently $M_2^2:M_2^3\sim 1:\kappa/q_2$. If the relative change in the potential over an electron wavelength is small the parameter κ/q_2 is small, and the term M_2^1 in (2.30) is dominant while M_2^2 and M_2^3 are first- and second-order corrections. This situation obtains in the semiclassical limit described by the Wentzel, Kramers, Brillouin, and Jeffreys (WKBJ) approximation, and to first order in κ/q_2 we have

$$M_2\approx M_2^1+M_2^2. \tag{2.37}$$

To this approximation, the evaluation of M_2 requires evaluating only single integrals as is the case for M_1 which occurs in the first-order effect. It is of interest to observe that the matrices M_1 and M_2^2 have the same form which makes first-order calculations partially useful for second-order calculations. The zeroth-order approximation, $M_2\approx M_2^1$, is equivalent to setting $E_j=E_0$ in (2.16b) as can be seen from comparing (2.31) to (2.16b).

If, on the other hand, the potential varies so rapidly in an electron wavelength that V' behaves like a delta function, the integrals for M_2^2 and M_2^3 become trivial and the integral for M_2^1 can be evaluated or estimated. We shall see from the examples of Sec. III that the three terms of (2.30) are comparable in magnitude, and Eq. (2.36)—which holds in the opposite extreme—still gives a reasonable estimate of M_2. We are led to conclude that Eq. (2.36) gives a good approximation for a slowly varying potential and a reasonable estimate for a general potential.

The formulation of this section will find applicability in discussing effects of third order or higher, however, we must then include in the perturbation the quadratic term in the vector potential. We remark also that by superposition we can treat the problem for any initial state of the electron gas and the radiation field. Such an initial state may be written as a coherent superposition of states of the type ψ_0 which has been here considered.

III. EXAMPLES

A. Semi-Infinite Square Well (SSW)

In this model $V(x)=-V_0$ for $x<0$ and zero for $x>0$. For a general positive energy we can determine the scattering matrix S by solving for the wave function[23] u or v of (2.18) and (2.19). Since we shall be concerned with electron states of energy E_r, as defined by (2.7) with r now taking the values 0, 1, and 2, we shall denote the corresponding S by S^r. The negative energy states, or "bound" states, are of the form u, except that q is replaced by ip where $p^2=-\mu E$, and the function u is divided by $\sqrt{2}$ which normalizes u to one in a unit length.[24] We easily find

$$S=\frac{1}{q+k}\begin{pmatrix}q-k & 2k\\ 2q & k-q\end{pmatrix}, \tag{3.1}$$

$$\phi_0=2^{-1/2}(e^{ik_0x}+S_{22}^0e^{-ik_0x},\ S_{12}^0e^{-p_0x}), \tag{3.2}$$

$$G(x,0)=-i\mu(k+q)^{-1}(e^{-ikx},e^{iqx}), \tag{3.3}$$

where the comma in (3.2) and (3.3) now separates negative and positive values of x.

[23] A solution for u determines S_{12} and S_{22}. The relations $qS_{12}=kS_{21}$, and $S_{11}S_{12}^*+S_{12}S_{22}^*=0$, discussed in the Appendix determine S_{11} and S_{21}.

[24] All energies $E>-V_0$ are allowed and there are no true bound states in this model. Since the matrix S has no poles for negative $E(q=ip)$, as can be seen from (3.1) we can use this matrix to describe all energy states.

Since $V'=V_0\delta(x)$, it follows immediately from the defining equations that:

$$\phi_1\sim-(\hbar\omega_\beta)^{-1}G_1(x,_0)V_0\phi_0(0),$$

or,

$$M_1=-(\hbar\omega_\beta)^{-1}V_0v_1(0)\phi_0(0), \tag{3.4}$$

$$M_2{}^2=iq_2(\hbar\omega_\beta)^{-2}V_0v_2(0)\phi_0(0), \tag{3.5}$$

$$M_2{}^3=(\hbar\omega_\beta)^{-2}V_0{}^2v_2(0)\phi_0(0)[G_1(0,0)-G_2(0,0)]$$
$$=-i(\hbar\omega_\beta)^{-2}V_0v_2(0)\phi_0(0)[k_1-q_1-(k_2-q_2)], \tag{3.6}$$

where the relation $\mu V_0=k_r{}^2-q_r{}^2$ has been used in (3.6).

The matrix $M_2{}^1$ reduces to evaluating the integral,

$$\int_{-\infty}^{0}v_2(x)\phi_0(x)dx,$$

which will be performed using the Wronskian of the two functions. Multiplying the wave equations,

$$v_2''+(q_2{}^2-U)v_2=0,$$
$$\phi_0''-(p_0{}^2+U)\phi_0=0,$$

by ϕ_0 and v_2, respectively, and subtracting we obtain:

$$(d/dx)W(v_2,\phi_0)=(q_2{}^2+p_0{}^2)v_2\phi_0=2\mu\hbar\omega_\beta v_2\phi_0,$$

and

$$2\mu\hbar\omega_\beta\int_{-\infty}^{0}v_2\phi_0dx=v_2(0)\phi_0'(0)-v_2'(0)\phi_0(0). \tag{3.7}$$

Since (2.19) and (3.2) give $v_2'(0)=-ik_2v_2(0)$, $v_2(0)=S_{21}{}^2$, $\phi_0'(0)=-p_0\phi_0(0)$, and $\phi_0(0)=S_{12}{}^0/\sqrt{2}$, we can write:

$$M_2{}^1=\tfrac{1}{2}V_0(\hbar\omega_\beta)^{-2}v_2(0)\phi_0(0)(-ik_2+p_0),$$

$$M_2=\frac{i\sqrt{2}V_0q_2k_0}{(\hbar\omega_\beta)^2(q_2+k_2)(k_0+ip_0)}(k_2-2k_1+2q_1-ip_0). \tag{3.8}$$

If $E_1<0$, q_1 in (3.8) is replaced by ip_1.

A comparison of (3.5), (3.6), and (3.7) shows that the three second-order matrix elements are all of the same order of magnitude, except near the threshold where q_2 is small and $M_2{}^2$ becomes negligible, which supports the arguments presented in the previous section. Also, the identity (2.35) can be easily verified.

Equations (3.4) and (3.8) are now used in (2.15) and (2.16) to obtain dI_1 and dI_2. The total current densities I_1 and I_2 are obtained by summing over the initial states. In general, an appropriate summation over the initial radiation states must be performed; however, we shall restrict the discussion here to one radiation oscillator, and sum only over the electron states. Appropriate to an electron gas in a metal at zero temperature, we multiply dI_r, $r=1$, 2, by $2(dk_0/\pi)\times(dk_ydk_z/4\pi^2)$ and integrate over the hemisphere $k_0{}^2+k_y{}^2+k_z{}^2=k_f{}^2$, $k_0>0$, where k_f is the radius of the usual Fermi sphere. It must be emphasized here that the quantization of the electron motion in the x direction does not follow from the semi-infinite potential model itself, it is rather a supplementary condition added to the model. In contrast, the finite-plate potential model has discrete bound states; and in the continuum limit, the number of electron states in the interval dk_0 per unit length, and for a given spin direction is given precisely by[25] dk_0/π. This difficulty will disappear when we describe in Sec. IV a limiting process by which the semi-infinite model is deduced from the finite model.

Using the fine structure constant α, the speed of light c, the Bohr radius a_B, the electron density N, and the radiation wavelength (divided by 2π) $\lambda\!\!\!^{-}_\beta$, and defining the energies $\mu^{-1}k_0{}^2$, $\hbar\omega_\beta$, and V_0, by $\epsilon\zeta$, $\Omega\zeta$, and $\eta\zeta$, respectively, where ζ is the Fermi energy $\mu^{-1}k_f{}^2$, we deduce the following transparent formulas for the current densities

$$I_1=\alpha^4(a_Bk_f)^3(6\pi Nec)(n_\beta\lambda\!\!\!^{-}_\beta{}^3)(\mathbf{e}_\beta\cdot\hat{x})^2J_1, \tag{3.9}$$

$$J_1=\frac{1}{2}\int^1(1-\epsilon)(\epsilon+\Omega-\eta)^{1/2}\epsilon^{1/2}\left(\frac{(\epsilon+\Omega)^{1/2}-(\epsilon+\Omega-\eta)^{1/2}}{(\epsilon+\Omega)^{1/2}+(\epsilon+\Omega-\eta)^{1/2}}\right)d\epsilon, \tag{3.10}$$

$$I_2=\alpha^7(a_Bk_f)^5(3\pi^2Nec)(n_\beta(n_\beta-1)\lambda\!\!\!^{-}_\beta{}^6)(\mathbf{e}_\beta\cdot\hat{x})^4J_2, \tag{3.11}$$

$$J_2=\frac{1}{2}\int^1(1-\epsilon)(\epsilon+2\Omega-\eta)^{1/2}\epsilon^{1/2}\left(\frac{(\epsilon+2\Omega)^{1/2}-(\epsilon+2\Omega-\eta)^{1/2}}{(\epsilon+2\Omega)^{1/2}+(\epsilon+2\Omega-\eta)^{1/2}}\right)$$
$$\times|(\epsilon+2\Omega)^{1/2}-2(\epsilon+\Omega)^{1/2}+2(\epsilon+\Omega-\eta)^{1/2}-i(\eta-\epsilon)^{1/2}|^2d\epsilon. \tag{3.12}$$

The lower limits of integration in the integrals J_r, $r=1$, 2, are determined by the condition $q_r>0$ or $\epsilon+r\Omega-\eta>0$. If $\epsilon+\Omega-\eta<0$ in (3.12), $(\epsilon+\Omega-\eta)^{1/2}$ is replaced by $i|(\epsilon+\Omega-\eta)^{1/2}|$. Note that $\alpha a_3k_f\equiv\hbar k_f/(mc)$.

Useful results can be derived near the threshold where the photoelectrons are excited from the vicinity of the Fermi surface. Define the energies ϵ_r and Ω_r by the relations, $\epsilon_r+r\Omega-\eta=0$, and $1+r\Omega_r-\eta=0$ for $r=1$, and 2. The lower limit of integration in J_r becomes ϵ_r and the integrals can be approximated by integrating only over $(1-\epsilon)(\epsilon-\epsilon_r)^{1/2}$ and setting $\epsilon=1$ in the

[25] This follows easily from Bohr's quantization rule. Mitchell (Ref. 14) has left out a factor 2 by using $(dk_0/2\pi)$ instead of dk_0/π. The factor 2 was restored by Makinson (see Ref. 5) but its origin became unclear after Makinson attributed it to the spin in his footnote on p. 377. The resolution of this rather trivial point is the following: states of negative k_0 are identical to those of positive k_0, and consequently the Fermi sphere of free electrons becomes in the presence of the surface a hemisphere with the spectrum twice as dense in the k_0 direction as it is in the k_y or k_z directions.

remaining terms. We have the equations

$$J_1 \approx (2/15)(1-\epsilon_1)^{5/2}[(1+\Omega)^{1/2}-(1-\epsilon_1)^{1/2}] \times[(1+\Omega)^{1/2}+(1-\epsilon_1)^{1/2}]^{-1}, \quad (3.13)$$

$$J_2 \approx (2/15)(1-\epsilon_2)^{5/2}[(1+2\Omega)^{1/2}-(1-\epsilon_2)^{1/2}] \times[(1+2\Omega)^{1/2}+(1+\epsilon_2)^{1/2}]^{-1}|(1+2\Omega)^{1/2}-2(1+\Omega)^{1/2} +i[2(\eta-\Omega-1)^{1/2}-(\eta-1)^{1/2}]|^2, \quad (3.14)$$

which imply that for Ω near the threshold frequency Ω_r, the photocurrent dependence on frequency is given by

$$I_1 \propto (\Omega-\Omega_1)^{5/2}\Omega^{-3}, \quad (3.15)$$

$$I_2 \propto (\Omega-\Omega_2)^{5/2}\Omega^{-6}. \quad (3.16)$$

From (3.14) we see that J_2 can be of order 10^{-3}. For $n_\beta\lambda_\beta^3=1$ which corresponds to $n_\beta=10^{15}$ cm^{-3} and $\lambda_\beta=(2\pi)10^3$ Å, Eq. (3.11) shows that for ordinary metals $I_2\sim 10^{-3}$ A/cm^2.

The current density I_1 is the same as given by Mitchell[14] (except for the factor 2). Equation (3.8) is equivalent to Eq. (43) of Smith[11] when the quantity $-2\beta_{1x}$ in that equation is replaced by $+2\beta_{1x}$. The material which follows Eq. (43) in Smith's paper suffers from many unfortunate errors, which we believe to have corrected here.

B. Linear Potential

Another simple potential for which the evaluation of M_1 and M_2[2] is immediate is defined by:

$$\begin{aligned} V(x) &= -V_0, \quad x\leq -a, \\ &= (V_0/2a)(x-a), \quad |x|\leq a \\ &= 0, \quad x\geq a. \end{aligned} \quad (3.17)$$

From the Wronskian property used in evaluating M_2^1 in Sec. IIIA, we have

$$\langle v_r^*|V'|\phi_0\rangle = V_0(2a\mu r\hbar\omega_\beta)^{-1}[W(v_r,\phi_0)]_{-a}^{a} \quad (3.18)$$

which shows that M_1 and M_2[2] are determined from the values of the wave functions and their derivatives at the points $x=\pm a$. These values are given in terms of the elements of the scattering matrix; for the wave functions have the same form as those discussed in Sec. IIIA with the comma now separating the regions $x\leq a$ and $x\geq a$ and thus apply at the points $x=\pm a$.

The scattering matrix is determined by solving for the wave function,

$$(e^{-ik(x+a)}, \quad Ce^{-iq(x-a)}+De^{iq(x-a)}).$$

In the region $|x|\leq a$, the solution is written as a combination of the Airy integrals Ai(z) and Bi(z), which we shall denote simply by $A(x)$ and $B(x)$, where x and z are related by $z=(\mu V_0/2a)^{1/3}(x-a-2aE/V_0)$. Denoting the values of $A(x)$ and $B(x)$, and their derivatives $A'(x)$ and $B'(x)$ at $x=\pm a$ by $A_\pm$, $B_\pm$, $A_\pm'$, and $B_\pm'$, we find by elementary methods that C and D are given by

$$\begin{pmatrix} C \\ D \end{pmatrix} = \frac{1}{2iqW(A,B)}\begin{pmatrix} iq & -1 \\ iq & 1 \end{pmatrix}\begin{pmatrix} A_+ & B_+ \\ A_+' & B_+' \end{pmatrix} \times\begin{pmatrix} B_-' & -B_- \\ -A_-' & A_- \end{pmatrix}\begin{pmatrix} 1 \\ -ik \end{pmatrix}, \quad (3.19)$$

where the Wronskian[26] $W(A,B)=(\mu V_0/2\pi^3 a)^{1/3}$. The scattering matrix is given by:

$$S_{11}=(D/C)e^{-2iqa}, \quad (q/k)S_{12}=S_{21}=e^{-i(k+q)a}/C, \quad S_{22}=-(S_{21}/S_{21}^*)S_{11}^*, \quad (3.20)$$

which completes the information necessary for a calculation of M_1 and M_2[1]. No numerical computations will be given here, since we hope to return to this problem in the future and discuss the first and second order matrix elements in the WKBJ limit.

C. Finite Square Well (FSW)

In this model,[12,13] $V(x)=-V_0$ for $|x|<a$, and $V(x)=0$ for $|x|>a$. We shall derive M_1 for this model to introduce the discussion of Sec. IV. The symmetric bound states ϕ_0^s and the antisymmetric states ϕ_0^a contribute the matrix elements M_1^s and M_1^a, respectively. If we define a symmetric, and an antisymmetric Green's function by

$$\begin{aligned} G^s(x,y) &= G(x,y)+G(x,-y), \\ G^a(x,y) &= G(x,y)-G(x,-y), \end{aligned} \quad (3.21)$$

and use (2.24) we obtain

$$\begin{aligned} \phi_1^a(x) &\sim -G_1^a(x,a)V_0\phi_0^s(a)(\hbar\omega_\beta)^{-1}, \\ \phi_1^s(x) &\sim -G_1^s(x,a)V_0\phi_0^a(a)(\hbar\omega_\beta)^{-1}, \end{aligned} \quad (3.22)$$

where $\phi_1^{s,a}(x)$ and $G_1^{s,a}(x,a)$ have the same symmetry.

It is evident that, for positive x,

$$G^s(x,a)=\mu(iq\cos ka+k\sin ka)^{-1} \times(\cos kx, \cos kae^{iq(x-a)}), \quad (3.23)$$

$$G^a(x,a)=\mu(iq\sin ka-k\cos ka)^{-1} \times(\sin kx, \sin kae^{iq(x-a)}),$$

where the comma separates the ranges $0<x<a$, and $x>a$, and symmetry considerations determine G^s and G^a for negative x. The poles of G^s and G^a for $q=ip$ are given by: $k\sin ka-p\cos ka=0$, and $k\cos ka+p\sin ka=0$. These poles determine the location of the symmetric and antisymmetric bound states, respectively, and it follows that[27] $\phi_0^s(a)$ or $\phi_0^a(a)=\pm a^{-1/2}k_0|k_0+ip_0|^{-1}$.

[26] We use the Airy integrals as defined in H. Jeffreys, Phil. Mag. 33, 451 (1942). In this definition, $W(\mathrm{Ai}(z),\mathrm{Bi}(z))=1/\pi$ and thus $W(A(x),B(x))=(1/\pi)(dz/dx)$. See also H. Jeffreys and B. Jeffreys, *Methods of Mathematical Physics* (Cambridge University Press, New York, 1956), p. 508.

[27] The propagation constants k_0 and p_0 are, of course, different for the symmetric and antisymmetric states. Here, these constants should be taken to mean the appropriate constants for the state under consideration.

To within an unimportant $\pm$ sign, we find from (3.22) and (3.23) that

$$M_1^{s,a}=-2k_0q_1V_0(\hbar\omega_\beta a^{1/2}|k_0+ip_0|)^{-1}\mathfrak{M}_1^{s,a},$$
$$\mathfrak{M}_1^{s}=i\sin k_1a(iq_1\sin k_1a-k_1\cos k_1a)^{-1}, \quad (3.24)$$
$$\mathfrak{M}_1^{a}=i\cos k_1a(iq_1\cos k_1a+k_1\sin k_1a)^{-1}.$$

For comparison, we write M_1 for the SSW taken from (3.4) after renormalizing ϕ_0 to one in the length $2a$, namely,

$$M_1=-2k_0q_1V_0[\hbar\omega_\beta a^{1/2}(k_0+ip_0)(q_1+k_1)]^{-1}. \quad (3.25)$$

First of all, if a and V_0 are of order unity in atomic units, or, more precisely, if $(\mu V_0)^{1/2}a$ is not a large number, the FSW has a small number of bound states. The normalization constant $a^{1/2}$ in (3.24) should be replaced by the exact factor $(a+1/p_0)^{1/2}$, and the matrix elements M_1^s and M_1^a are used in the usual way to calculate currents or cross sections. Evidently, in this limit, the FSW and SSW models are quite different.

However, we are interested here in the limit of very large $(\mu V_0)^{1/2}a$ which will permit a comparison of the two models. The essential differences are that $\mathfrak{M}_1$ (used for $\mathfrak{M}_1^{s,a}$) of (3.24) is replaced by $(q_1+k_1)^{-1}$ in (3.25), and that $\mathfrak{M}_1$ and $|\mathfrak{M}_1|^2$ are periodic in k_1a, and as $k_1a\to\infty$, neither $\mathfrak{M}_1$ nor $|\mathfrak{M}_1|^2$ tend to a definite limit unless the limit is taken in the Abel sense. The Abel limit for a periodic function $f(x)$ as $x\to\infty$ is given by

$$\lim_{x\to\infty}f(x)=\lim_{\epsilon\to0}\epsilon\int_0^\infty e^{-\epsilon x}f(x)dx=\frac{1}{2\pi}\int_0^{2\pi}f(x)dx, \quad (3.26)$$

where the last equality follows from expanding $f(x)$ in a Fourier series. The Abel limit is thus obtained by taking the average of the function, $\langle f\rangle$. We have two possible interpretations based on averaging $\mathfrak{M}_1$ or $|\mathfrak{M}_1|^2$.

If we apply (3.26) to $\mathfrak{M}_1$ and make the substitution, $e^{ik_1a}=z$, we obtain that

$$\langle\mathfrak{M}_1\rangle=(2\pi i)^{-1}\int_C\mathfrak{M}_1(z)dz/z,$$

where the contour of integration C is the unit circle. For real q_1, $\mathfrak{M}_1$ is analytic in z for $|z|\leq1$, and we have

$$\langle\mathfrak{M}_1^{s}\rangle=\langle\mathfrak{M}_1^{a}\rangle=\mathfrak{M}_1(0)=(q_1+k_1)^{-1}, \quad (3.27)$$

which is precisely what we need to establish the equivalence of the FSW and SSW matrix elements. In this sense, the SSW can be looked upon as a FSW for which $k_1a\to\infty$, and hence the two models share the quantization rule of the FSW which reduces in the continuum limit to the rule previously discussed in Sec. IIIA. Thus the difficulty of the bound states in the SSW model is removed.

If, on the other hand, we follow Sommerfeld and Bethe,[13] and insert $|M_1^{s,a}|^2$ in (2.15a), and then average $|\mathfrak{M}_1^{s,a}|^2$ we obtain by a contour integration that

$$\langle|\mathfrak{M}_1^{s}|^2\rangle=\langle|\mathfrak{M}_1^{a}|^2\rangle=[q_1(q_1+k_1)]^{-1}, \quad (3.28)$$

which is a factor $(q_1+k_1)/q_1$ larger than the SSW value $(q_1+k_1)^{-2}$. The current density I_1 based on (3.28) is given by (3.9) with J_1 of (3.10) replaced by

$$J_1=\frac{1}{2}\int^1(1-\epsilon)\epsilon^{1/2}[(\epsilon+\Omega)^{1/2}-(\epsilon+\Omega-\eta)^{1/2}]d\epsilon. \quad (3.29)$$

Near the threshold (3.29) and (3.10) give

$$J_1\approx\tfrac{1}{4}(1-\epsilon_1)^2[(1+\Omega)^{1/2}-(1-\epsilon_1)^{1/2}], \quad (3.30)$$
$$I_1\propto(\Omega-\Omega_1)^2\Omega^{-3}, \quad (3.31)$$

in contrast to (3.13) and (3.15) of the SSW. The results given in Eqs. (3.28)–(3.31) agree with those of Sommerfeld and Bethe,[13] except for some minor differences.

We shall argue that the first limiting procedure which deals with the average of the matrix element itself, and not its square, is the correct procedure. This procedure is essentially based on cutting off the "spatial" oscillations in the amplitude of the outgoing wave, $\exp iq(x-a)$, in Eq. (3.23). Such oscillations, being in essence a "memory" of the surface barrier at $x=-a$, can not survive as the separation of the two surface barriers becomes sufficiently large. This, in spirit, is not different from the cutoff applied to the "temporal" factor $\exp(-iEt/\hbar)$ in the wave function as $t\to\pm\infty$. Indeed such a cutoff was used in the derivation[6,7] of the basic equation (2.3). We shall now proceed to generalize the results of the equivalence of the two potential models to more involved potentials than square wells.

IV. EQUIVALENCE OF MODELS

An examination of Eqs. (2.24)–(2.27), or (2.5) and (2.6), shows that the averages $\langle M_1\rangle$ and $\langle M_2\rangle$ are strongly related to the averages $\langle G_1(x,y)\rangle$ and $\langle G_1(x,y)G_2(y,z)\rangle$. We shall now investigate the average $\langle G(x,y)\rangle$ for the finite plate potential defined by

$$\begin{aligned}V(x)&=-V_0, && -2a<x<0,\\ &=V_1(x) && x>0,\\ &=V_2(-2a-x), && x<-2a,\end{aligned} \quad (4.1)$$

where the origin has been chosen for convenience, near the surface from which electron emission is observed, and where the two barriers, V_1 and V_2, which need not be the same, rise to zero in a distance much less than a.

The problem will essentially reduce to identifying certain averages as elements of the scattering matrix for the semi-infinite potential obtained from (4.1) by setting $V_2=-V_0$. Let us denote this matrix by Σ, and reserve the symbol S to the scattering matrix of the potential V itself. Denoting the two solutions of Schrödinger's equation for the potential $V_r(x)$, $r=1, 2$, which behave asymptotically as e^{iqx} and e^{-iqx} by $f_r(x)$

and $g_r(x)$, respectively, we can write Σ for future reference, in terms of the values of f_1, g_1, and their derivatives f_1' and g_1' at the origin, namely,[23]

$$\Sigma=\frac{1}{f_1'(0)+ikf_1(0)} \times\begin{pmatrix}-ikg_1(0)-g_1'(0) & 2ik\\ 2iq & -f_1'(0)+ikf_1(0)\end{pmatrix}. \quad (4.2)$$

Let us begin the discussion with the symmetric potential for which $V_1=V_2$ in (4.1), and the line $x=-a$ is a line of symmetry.

A. Symmetric Potential

The symmetry of the potential imposes that we work with symmetric and antisymmetric wave functions and Green's functions, and that these functions need be defined only over the range $x\geq -a$. It is clear that, for example, the term $G_2V'G_1V'\phi_0$ in (2.27) can be written as,

$$\int_{-a}^{\infty}\int_{-a}^{\infty} G_2^{s}(x,y)V'(y)G_1^{a}(y,z)V'(z)\phi_0^{s}(z)dydz,$$

or (4.3)

$$\int_{-a}^{\infty}\int_{-a}^{\infty} G_2^{a}(x,y)V'(y)G_1^{s}(y,z)V'(z)\phi_0^{a}(z)dydz,$$

depending on the symmetry of the bound state, where now

$$G^{s,a}(x,y)=G(x,y)\pm G(x,-2a-y),$$
$$\phi_0^{s,a}(x)=\pm\phi_0^{s,a}(-2a-x). \quad (4.4)$$

For positive energy we can define symmetric and antisymmetric states by

$$\phi^{s}(x)=(\cos k(x+a),\ \Lambda_s f_1(x)+\Lambda_s^{*}g_1(x)),$$
$$\phi^{a}(x)=(\sin k(x+a),\ \Lambda_a f_1(x)+\Lambda_a^{*}g_1(x)),$$
$$\Lambda_s=(i/2q)[g_1'(0)\cos ka+kg_1(0)\sin ka],$$
$$\Lambda_a=(i/2q)[g_1'(0)\sin ka-kg_1(0)\cos ka], \quad (4.5)$$

where the comma is at the origin, the star denotes as usual the complex conjugate, and $g_1(x)=f_1^{*}(x)$ for real q. The bound states correspond to the zeros of $\Lambda_{s,a}^{*}$ for $q=ip$, and have the form (4.5) multiplied by the normalization constant $a^{-1/2}$.

$G^{s,a}$ is now constructed from the functions u of (2.18) and $\phi^{s,a}$ of (4.5), and the result is

$$G^{s,a}(x,y)=(\mu/2iq\Lambda_{s,a}^{*}S_{12})[\phi^{s,a}(x)u(y) \text{ and } \phi^{s,a}(y)u(x)] \text{ for } x<y \text{ and } x>y. \quad (4.6)$$

Since u/S_{12} is determined completely by the semi-infinite potential (SIP) and can be written as

$$u(x)/S_{12}=(1/\Sigma_{12})(e^{ikx}+\Sigma_{22}e^{-ikx},\ \Sigma_{12}f_1(x)), \quad (4.7)$$

we have to concern ourselves only with the average $\langle\phi^{s,a}/\Lambda_{s,a}^{*}\rangle$. From (4.5) the averages needed are $\langle\cos k(x+a)/\Lambda_s^{*}\rangle$, $\langle\Lambda_{s,a}/\Lambda_{s,a}^{*}\rangle$, and $\langle\sin k(x+a)/\Lambda_a^{*}\rangle$.

These averages are performed using the unit circle contour of Sec. IIIC. For positive energy (real q) the functions to be averaged are analytic functions of the complex variable, $z=e^{ika}$, for $|z|\leq 1$. If $F(z)$ represents any of these functions we have the simple result,

$$\langle F(z)\rangle=(2\pi i)^{-1}\int_C F(z)dz/z=F(0). \quad (4.8)$$

Using (4.5), (4.8), and (4.2) we have

$$\langle\cos k(x+a)/\Lambda_s^{*}\rangle=\frac{2q}{2\pi}\int_C\frac{e^{-ikx}z^{-1}+e^{ikx}z}{f_1'(0)(z+z^{-1})-ikf_1(0)(z-z^{-1})}\frac{dz}{z}$$
$$=2iq[f_1'(0)+ikf_1(0)]^{-1}e^{-ikx}=\Sigma_{21}e^{-ikx}, \quad (4.9)$$

$$\langle\Lambda_s/\Lambda_s^{*}\rangle=\frac{-1}{2\pi i}\int_C\frac{g_1'(0)(z+z^{-1})-ikg_1(0)(z-z^{-1})}{f_1'(0)(z+z^{-1})-ikf_1(0)(z-z^{-1})}\frac{dz}{z}=\Sigma_{11}, \quad (4.10)$$

And similarly,

$$\langle\sin k(x+a)/\Lambda_{a}^{*}\rangle=\Sigma_{21}e^{-ikx}, \quad (4.11)$$

$$\langle\Lambda_a/\Lambda_{a}^{*}\rangle=\Sigma_{11}. \quad (4.12)$$

Thus,

$$\langle\Lambda_{s,a}^{*-1}\phi^{s,a}(x)\rangle=(\Sigma_{21}e^{-ikx},\ \Sigma_{11}f_1(x)+g_1(x)), \quad (4.13)$$

where the right-hand side is the function $v(x)$ for the SIP, and we conclude that

$$\langle G^{s,a}(x,y)\rangle=G(x,y) \quad \text{for the SIP.} \quad (4.14)$$

It is important to observe that the averaging process removes the distinction between G^s and G^a, and eliminates the incoming wave e^{ikx} in (4.9) and (4.11) which amounts to neglecting the wave reflected from the boundary at the left.

For negative energies ($q=ip$), f_1 and g_1 are real and two simple poles appear in the integrands of (4.9) and (4.10) corresponding to the zeros of Λ^{*}_s which are given by $z_s^{2}=-[f_1'(0)+ikf_1(0)][f_1'(0)-ikf_1(0)]^{-1}$ and which indicate the appearance of two bound states. Similarly, two poles appear in the integrands of (4.11) and (4.12) at $z_a^{2}=-z_s^{2}$. Since these poles lie on the unit circle $|z|=1$, the path of integration has to be modified for negative energies. The definition $G=(E-H_e+i\epsilon)^{-1}$ assigns a small negative imaginary part to the poles of G, and consequently the values of k corresponding to the bound states, namely, $k_0=k_0^{(1)}$, $k_0^{(2)}$, etc., must be understood as $k_0-i\epsilon$. The transformation $z=e^{ika}$ pushes these poles slightly outside the unit circle. Therefore,

the contour C in (4.8)–(4.13) must be dented, if necessary, to place outside the contour of integration any poles such as z_s and z_a which occur at $|z|=1$. With this modification in the path of integration C, *Eq. (4.8) becomes the fundamental equation of the averaging process for negative and positive energies.* Equations (4.9)–(4.14) apply now to all energies.

We shall now extend the results of Sec. IIIC to this model. In taking the average of the matrix elements $M_1^{s,a}$ and $M_2^{s,a}$ (contributed by $\phi_0^{s,a}$) we must leave the bound states intact[28] and average only the Green's functions. Since $\langle M_1^{s,a}\rangle$ involves only $\langle G_1^{s,a}\rangle$ we obtain, using (4.14), the results of the SIP. Similarly, the terms in $\langle M_2^{s,a}\rangle$ which contain only $\langle G_2^{s,a}\rangle$ reduce to the corresponding terms of the SIP, and we must deal with those terms in $M_2^{s,a}$ which contain two Green's functions, namely, $G_2V'G_1V'\phi_0$ which has been given explicitly in (4.3), and $G_2V'G_2V'\phi_0$ of (2.27). Now $G_2^{s,a}$ and $G_1^{s,a}$ are periodic in k_2a and k_1a, respectively, which can be treated as two independent variables for averaging purposes, and we simply obtain that the average of the product $\langle G_2^{s,a}:G_1^{s,a}\rangle$, reduces to the product of the averages, namely, $\langle G_2^{s,a}\rangle:\langle G_1^{s,a}\rangle$ which brings us back to the SIP; the colon here denotes that an operator such as V' separates the two Green's functions.

From the symmetry of the problem the term $G_2V'G_2V'\phi_0$ brings the product $G_2^s:G_2^a$ which is periodic in the variable k_2a. Performing the average in the complex plane of e^{ik_2a} we find using (4.8) that $\langle G_2^s:G_2^a\rangle=\langle G_2^{s,a}\rangle:\langle G_2^{s,a}\rangle$ which is equivalent to the SIP result.

Thus to second order, the results of the symmetric and the SIP models are identical, and in fact the results can be extended to higher order.[29]

B. General Potential

The potential is now defined by (4.1) with $V_2\neq V_1$. The relevant $G_1(x,y)$ is given by (2.20) and we must now solve for the functions $u(x)/S_{12}$ and $v(x)$. We find by elementary methods that

$$u(x)/S_{12}=Af_2(x+2a)+Bg_2(x+2a),\qquad \alpha e^{ikx}+\beta e^{-ikx},\quad f_1(x),$$

for

$$x\leq -2a,\quad -2a\leq x\leq 0,\quad x\geq 0,$$

respectively, where

$$\begin{aligned}A&=(4kq)^{-1}\{[g_2'(0)-ikg_2(0)][f_1'(0)+ikf_1(0)]e^{-2ika}\\&\quad-[g_2'(0)+ikg_2(0)][f_1'(0)-ikf_1(0)]e^{2ika}\},\\B&=(4kq)^{-1}\{[-f_2'(0)+ikf_2(0)][f_1'(0)+ikf_1(0)]e^{-2ika}\\&\quad+[f_2'(0)+ikf_2(0)][f_1'(0)-ikf_1(0)]e^{2ika}\},\\\alpha&=(2ik)^{-1}[f_1'(0)+ikf_1(0)],\\\beta&=-(2ik)^{-1}[f_1'(0)-ikf_1(0)].\end{aligned}\tag{4.15}$$

The scattering matrix S and the function $v(x)$ can now be written down[23]:

$$S=\begin{pmatrix}-B^*/A & e^{-2iqa}/A\\ e^{-2iqa}/A & (B/A)e^{-4iqa}\end{pmatrix},\tag{4.16}$$

$$\begin{aligned}&v(x)=A^{-1}g_2(x+2a),\\&\gamma e^{ikx}+\delta e^{-ikx},\quad S_{11}f_1(x)+g_1(x),\end{aligned}\tag{4.17}$$

for $x\leq -2a$, $-2a\leq x\leq 0$, $x\geq 0$, respectively; the coefficients γ and δ are given by

$$\begin{aligned}\gamma&=[g_2'(0)+ikg_2(0)][2ikA]^{-1}e^{2ika},\\\delta&=[-g_2'(0)+ikg_2(0)][2ikA]^{-1}e^{-2ika}.\end{aligned}\tag{4.18}$$

We are now ready to discuss the averages $\langle M_1\rangle$ and $\langle M_2\rangle$ for this model. From (2.29) or (2.15b) we see that $\langle M_1\rangle$ depends only on $\langle v_1\rangle$. Applying (4.8) to (4.17) we have:

$$\begin{aligned}\langle\gamma\rangle&=\langle 1/A\rangle=0,\\\langle\delta\rangle&=\frac{(4kg)[-g_2'(0)+ikg_2(0)]}{(2ik)[g_2'(0)-ikg_2(0)][f_1'(0)+ikf_1(0)]}=\Sigma_{21},\\\langle S_{11}\rangle&=-\langle B^*/A\rangle\\&=-\frac{[g_2'(0)-ikg_2(0)][g_1'(0)+ikg_1(0)]}{[g_2'(0)-ikg_2(0)][f_1'(0)+ikf_1(0)]}=\Sigma_{11},\end{aligned}\tag{4.19}$$

which means that $\langle v_1\rangle$ is zero for $x\leq -2a$ and coincides with the SIP function for $x>-2a$. Letting $a\to\infty$, $\langle M_1\rangle$ assumes the SIP value.

To discuss $\langle M_2\rangle$ it is simplest to work with the definition (2.16b) which gives the average $\langle v_2(x):G_1(x,y)\rangle$. Averaging $v_2(x)$ first introduces a cutoff in x for $x<-2a$ which means that $\langle G_1(x,y)\rangle$ has to be considered only for $x>-2a$. This amounts to leaving the function u_1/S_{12} intact and averaging only[30] v_1 which introduces again a cutoff now in y for $y<-2a$. The barrier V_2 has thus been eliminated and as $a\to\infty$ we are left with the SIP model with one barrier, namely, V_1. Clearly, the procedure applies to higher order matrix elements[29]

[28] The exact location of the bound states, namely, the exact values of k_0 and p_0 are of no great interest in the continuum limit, only the density of states as given by the rule dk_0/π is important. In both the finite and the SIP models ϕ_0 has the same behavior at the barrier and that influences the matrix elements in the same way.

[29] This conclusion has to be somewhat qualified, for in considering the average $\langle G_r:G_{r-1}:\cdots G_1\rangle$ it is possible that for certain bound-state energies an angle, say, k_na is an integral multiple of another angle k_ma, and, hence, these two variables are no longer independent, and the average of the product may fail to yield the product of the averages. This possibility arises, the earliest, in fifth order, for if $k^2/\mu=\hbar\omega_\beta/3$ we have $k_\beta a=2k_1a$. Using (4.9)–(4.12), and performing the average in the complex plane $z=e^{ik_ma}$, it is simple to show that for the symmetric potential we will obtain $\langle G_n^{s,a}:G_m^{s,a}\rangle=\langle G_n^{s,a}\rangle:\langle G_m^{s,a}\rangle$. However, we have not succeeded in extending this result to the general potential of Sec. IVB.

[30] For negative energy, A has four zeros on $|z|=1$ as can be seen from (4.15). Eqs. (4.19) remain valid when the path of integration is modified as in Sec. IVA.

and the equivalence of models extends to other perturbations.

In brief, two surface barriers are necessary to introduce the correct quantization rule; but as the separation of the two surfaces becomes large, each surface displays surface phenomena characteristic of its own barrier and independent of the other surface barrier, a result which is taken for granted in the SIP model but which we find hard to justify without resorting to the averaging procedure we have discussed.[31]

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APPENDIX

The orthogonality of the functions u and v of (2.18) and (2.19) follows directly from the properties of the scattering matrix S defined by (2.17). The time reversal symmetry (complex conjugation of the wave equation), and the conservation of current yield the relations $SS^*=I$, and $qS_{12}=kS_{21}$, where I is the identity matrix.[32] Using these properties, and the relation, $\delta(k-k')=(k/q)\delta(q-q')$, we have:

$$\begin{aligned}\langle u(q)\,|\,v(q')\rangle &= \pi[S_{11}S_{12}{}^*\delta(q-q')+S_{21}S_{22}{}^*\delta(k-k')] \\ &= \pi(SS^*)_{12}\delta(q-q')=0\,,\end{aligned} \tag{A1}$$

which is the desired result. Similarly, we obtain:

$$\langle u(q)\,|\,u(q')\rangle = 2\pi(k/q)\delta(q-q')\,, \tag{A2}$$

$$\langle v(q)\,|\,v(q')\rangle = 2\pi\delta(q-q')\,. \tag{A3}$$

[31] The averaging procedure can be used to eliminate a boundary condition in problems of higher dimensionality. In three dimensions we can write the Green's function $G(r,0)$ for a point source at the origin as

$$\mu\sin k(r-a)/(4\pi r\sin ka), \quad \text{or} \quad \mu\cos k(r-a)/(4\pi r\cos ka)$$

with G satisfying obvious boundary conditions on the surface of the sphere $r=a$. Letting $a\to\infty$ and using (4.8) we obtain $\langle\sin k(r-a)/\sin ka\rangle=\langle-\cos k(r-a)/\cos ka\rangle=-e^{ikr}$ which is the free space function, and we have $\langle G(r,0)\rangle=-\mu\exp(ikr)/(4\pi r)$.

[32] When $q=k$ (finite potential) $S^\dagger=S^*$ and S is unitary. If in addition $V(x)=V(-x)$, $S_{11}=S_{22}$.

The method of the variation of constants, as used by Mitchell[14] and others, is essentially equivalent to expanding Green's function in eigenfunctions of the electron Hamiltonian H_e. The perturbation is turned on adiabatically at time $t\to-\infty$, and the amplitudes of the eigenfunctions are examined at $t=0$. We have for the usual time integral the relation,

$$\left(\frac{1}{i\hbar}\right)\int_{-\infty}^{0} e^{-i(E-H_e)t/\hbar}dt=(E-H_e+i\epsilon)^{-1}\equiv G. \tag{A4}$$

Expanding G in eigenfunctions of H_e using (A2) and (A3), we have the asymptotic relation,

$$G(x,y)\sim\frac{\mu}{2\pi}\left\{\frac{q}{k}\int_0^\infty\frac{u(q',x)u^*(q',y)}{q^2-q'^2+i\epsilon}dq' + \int_0^\infty\frac{v(q',x)v^*(q',y)}{q^2-q'^2+i\epsilon}dq'\right\}. \tag{A5}$$

However, for large x, only the outgoing waves in $u(q',x)$ and $v(q',x)$ survive, for using (A4) we have

$$\begin{aligned}e^{iq'x}(q^2-q'^2+i\epsilon)^{-1}\equiv -i\int_{-\infty}^{0} e^{-i(q^2-q'^2)(t+x/q')+i(q^2/q')x}dt \\ =-i\int_{-\infty}^{\infty} e^{-i(q^2-q'^2)z}dz e^{i(q^2/q')x} \\ =-2\pi i\delta(q^2-q'^2)e^{iqx}\end{aligned}$$

and

$$e^{-iq'x}(q^2-q'^2+i\epsilon)^{-1}\sim 0. \tag{A6}$$

Using (A6) and the definition of u and v in (A5) we find

$$G(x,y)\sim(\mu/2iq)e^{iqx}[(q/k)S_{12}u^*(q,y)+S_{11}v^*(q,y)]. \tag{A7}$$

The function inside the bracket in (A7) can be identified as $v(q,y)$ using the properties of S. We conclude that,

$$G(x,y)\sim(\mu/2iq)e^{iqx}v(y)\,, \tag{A8}$$

which is Eq. (2.14).