Green function and phase-shift multiple-reflection theory for electronic surface states

LETTER TO THE EDITOR

Green function and phase-shift multiple-reflection theory for electronic surface states

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Abstract. A more unified approach to the Bohr-like quantisation condition for the existence of electronic surface states within the multiple-reflection theory is discussed. It consists in employing the path-integral method to construct a WKB-like Green function. Simple calculations of the local density of states for image-induced surface resonances are also presented.

In the past few years the multiple-reflection (MR) theory originally developed by Echenique and Pendry [1] has been successfully applied to provide, predict and characterise a uniform picture of the crystal-induced (Shockley) and barrier (image)-induced electronic surface states in metals [2–4]. The present letter attempts to extend this approach applying the path-integral approximation method to construct a WKB-like Green function for a quantum well. To describe it, let us first present in brief the results of [1].

A crystal is arbitrarily terminated at some plane z_C (figure 1). On this plane the potential is the same as in the bulk crystal

$$V_C(z) = V_{Cr}(z) + iV_{Ci} \qquad i = (-1)^{1/2} \tag{1}$$

where V_{Ci} is a small imaginary contribution to the inner potential V_C and simulates damping effects in the crystal. Outside the adjustable image plane z_B, the potential is assumed to have an image form $V_B(z) = [4(z - z_i)]^{-1}$, where corrugation effects are negligible, i.e., $V_B(r, E) = V_B(z, E)$ and Im $V_B(z) = 0$ for simplicity. For z smaller than z_B the z-dependent surface potential is approximated by a constant value V. If $R_C = r_C e^{i\phi_C}$ and $R_B = r_B e^{i\phi_B}$ represent the reflectance of the electron wave at the crystal and surface barrier, respectively, the total amplitude of the wave after an infinite number of reflections is [1]

$$[1 - r_C r_B \exp\{i[\phi_C + \phi_B + 2k(z_B - z_C)]\}]^{-1} \tag{2}$$

where k is defined inside the well and (using atomic units throughout) $k = [2(E - V)]^{1/2}$. A pole in (2) corresponds to a bound surface state so the following condition must be satisfied

$$r_C = r_B = 1 \tag{3}$$

$$\phi_C + \phi_B + 2k(z_B - z_C) = 2\pi n \tag{4}$$
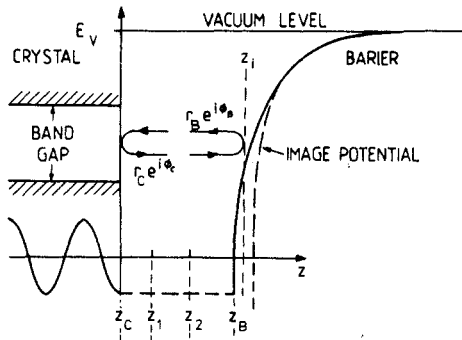
Figure 1. Potential profile of a semi-infinite crystal $(z < z_C)$ subject to the image potential $(z > z_B)$; z_i is the image plane. The surface states arise through multiple reflection between the terminating plane of the crystal and the surface barrier.
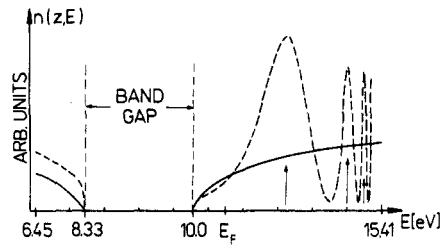

Figure 2. Surface density of states $n(z; E)$ for the image (broken curve) and for the step potential barrier (full curve); $z = z_C = z_B = 0$. Arrows indicate the image-induced surface resonances.

where n is an integer. The Bohr-like quantisation condition of the round trip phase accumulation ϕ (equation (4)) enables us to distinguish between barrier-induced (ϕ_B) and crystal-induced (ϕ_C) surface states, depending on the phase factor governing the resonance condition. Equation (3) requires both the absence of damping processes (Im $V_C = 0$), and the energies E in a relative bulk band gap ($r_C = 1$) as well as below the vacuum level ($r_B = 1$). If E extends out of these ranges or inelastic processes are taken into account, the stationary condition (3) and (4) must be replaced by the weaker one [4]

$$|1 - r_C r_B \exp\{i[\phi_C + \phi_B + 2k(z_C - z_B)]\}|^2 \to \text{MIN}. \tag{5}$$

Quite recently the stationary condition has been used to determine the energy of overlayer states [5], where ϕ_C and $2k(z_B - z_C)$ in equations (2) and (4) represent the phase shifts at the substrate–adsorbate interface and across the adsorbed metal film, respectively.

The purpose of this letter is to construct and to analyse a fixed energy Green function for a one-electron Hamitonian H in the position representation

$$G(z_1, z_2, k_\parallel = 0; E) = i\langle z_1|(E - H)^{-1}|z_2\rangle/2\pi \tag{6}$$

for z_1, z_2 inside the well (figure 1), and $H = T + V_S$, where T is the kinetic energy and V_S the potential energy of the system. The idea is that the Green function (6) can be defined in the semi-classical approximation in terms of a sum over all possible paths which connect points z_1 and z_2 [6]

$$G(z_1, z_2; E) = \{i/[2\pi(k(z_1)k(z_2))^{1/2}]\} \sum_{\text{paths}} \prod_m f_m \tag{7}$$

where $k(z) = [2(E - V(z))]^{1/2}$ is the local wavenumber defined inside the well, while f_m

are the factors associated with each path connecting z_1 and z_2. In a classically allowed region

$$f_m = \exp\left(i\bigg|_{z_1} \int^{z_2} k(z)\,dz\bigg|\right). \tag{8}$$

Taking into account all possibilities of reflections at the boundaries (R_C, R_B) and according to (7) the Green function for the quantum well may be expressed in the form

$$G(z_1, z_2; E) = (i/2k\pi)\,(\exp[ik(z_2 - z_1)] + R_C R_B \exp\{ik[2(z_B - z_C) + z_1 - z_2]\}$$
$$+ \exp[ik(z_B - z_C)]\,[R_C \exp\{ik[z_1 + z_2 - (z_B - z_C)]\}$$
$$+ R_B \exp\{-ik[z_1 + z_2 - (z_B - z_C)]\}]\,)\,\{1 - R_C R_B \exp[ik2(z_B - z_C)]\}^{-1} \tag{9}$$

where the geometric series has been summed.

The discrete energy spectrum of the system is determined by the poles of the propagator $G(z_1, z_2; E)$ [7] and for the energies E in the bulk band gap below the vacuum level E_v

$$|R_C| = r_C = |R_B| = r_B = 1 \tag{10a}$$

hence

$$R_C = \exp(i\phi_C) \qquad R_B = \exp(i\phi_B) \tag{10b}$$

and

$$1 - \exp\{i[\phi_C + \phi_B + 2k(z_B - z_C)]\} = 0. \tag{10c}$$

It is easy to see that the conditions (10a–c) for the existence of the true surface states are identical to those obtained from the MR theory ((2) and (4)).

In the continuum part of the energy spectrum (allowed energy bands and a region above the vacuum level) the existence of bounded states is not connected with the singularity of (9). Hence, a quantity of considerable physical interest is the density of states determined by the imaginery part of the Green function. For $z_1 = z_2 = z$ the local density of states (LDS) is defined as [7]

$$n(z; E) = -\text{Im}(\langle z|(E - H)^{-1}|z\rangle)/\pi. \tag{11}$$

Following from (9) and (11), the expression for the LDS in our system is

$$n(z; E) = (1/2k\pi^2)\,[1 - (r_C r_B)^2 + r_C(1 + r_B^2)\cos(2kz + \phi_C)$$
$$+ r_B\{\cos[2k(b - z) - \phi_B] + r_C^2\cos[2k(b - z) + \phi_B]\}]$$
$$\times |1 - r_C r_B \exp[i(\phi_C + \phi_B + 2kb)]|^{-2} \tag{12}$$

where $b = z_B - z_C$, while R_C and R_B from (9) are replaced by $r_C e^{i\phi_C}$ and $r_B e^{i\phi_B}$, respectively.

It is easy to see that the non-stationary condition in the MR approach (4) is reproduced in (12) explicitly, i.e., the minima of (4) appear to be the maxima in the LDS.

The Green function provides the appropriate theoretical tool for treating many-body effects (or lifetime effects), $\text{Im}\,V_C \neq 0$. The one-electron Green function reads simply (see (1) and (6)).

$$G(E) = (E - T - V_C)^{-1} = (E - T - V_{Cr} - iV_{Ci})^{-1} \tag{13}$$

so that introduction of the imaginary component V_{Ci} to V_C is equivalent to replacement

of E by $E - iV_{Ci}$ in the Green function for an undamped system, Im $V_C = 0$. In the formulation presented here the absorption effects of the crystal introduce an imaginary component into the phase of the crystal reflectivity ϕ_C. With the use of linear approximation the complex energy dependence of ϕ_C can be expressed in the form

$$r_C \exp\{i[\phi_C(E \mp iV_{Ci})]\} = \exp[i(\phi_C + i(\ln r_C \mp V_{Ci} \, \partial\phi_C/\partial E)]. \tag{14}$$

Thus, the LDS function (12) describes the damped surface states inside the energy gap (Im $V_C \neq 0$) and the surface resonances outside the gap. However, outside the energy gap an electron beam can lose flux due to diffraction processes, so that $r_C < 1$ even in the absence of the absorption effects. In this case the imaginary part of the phase shift $\phi_C(E)$ in (14) is reduced to $-\ln r_C$, where

$$r_C = [(ik\Psi(z_C) + \Psi'(z_C))/(ik\Psi(z_C) - \Psi'(z_C))] < 1 \tag{15}$$

and Ψ represents the crystal wave function; the prime indicates differentiation [8].

Simple calculations of the local surface density of states (Im $V_C = 0$, equations (12), (14), (15) and (16)) have been performed for the one-interface model, i.e. $z = z_C = z_B = 0$, and crystal parameters corresponding to the Al(001) face (4.41 eV—the work function, 11 eV—the Fermi level and 4.04 Å—the lattice constant). The wave function Ψ in (15) was determined from the two-band model (nearly free electron approximation) [2, 4, 9] and in the energy region outside the band gap the phase shift $\phi_C = $ constant [2, 4].

In the vacuum the surface potential barrier in the simplest case can be determined as ($r_B = 1$)

$$\phi_B/\pi = [3.4 \, \text{eV}/(E_V - E)]^{1/2} - 1 \tag{16a}$$

$$\phi_B = 2 \tan^{-1}\{-[(E_V - E)/E]^{1/2}\} \tag{16b}$$

for the image potential and for the step potential barrier, respectively [2].

Results of the calculation are presented in figure 2. In the near vicinity of the energy gap (8.33–10.0) eV a characteristic $E^{-1/2}$ dependence of the surface LDS is conserved independently of the surface potential shape. The effect of the image potential on the LDS (broken curve in figure 2) becomes significant in the energy region above the energy gap up to the vacuum level E_V. Maxima on the LDS curve represent the image-induced surface resonances, while the inverse of the half-width of the peak is proportional to the lifetime of an electron in this state. As can be seen, the higher the energy of the resonance, the longer the lifetime of this state.

To our knowledge, the LDS calculation performed within the extended phase-shift multiple-reflection theory presented above has not appeared in the literature before. The results obtained are in good agreement with the previous theoretical description [9] of the image-induced surface resonances measured recently in the inverse photoemission experiment [10, 11]. We believe that the more precise determination of the scattering characteristics of the crystal (R_C) and the surface barrier (R_B) in the extended MR theory presented here may give a convenient and powerful method for theoretical investigations of a wide class of the electronic surface states in metals.

References

[1] Echenique P M and Pendry J B 1978 *J. Phys. C: Solid State Phys.* **11** 2025
[2] Smith N V 1985 *Phys. Rev.* B **32** 3549
[3] Hulbert S L, Johnson P D, Weinert M and Garret R F 1986 *Phys. Rev.* B **33** 760
[4] Borstel G and Thorner G 1987 *Surf. Sci. Rep.* **8** 1
[5] Lindgren S A and Wallden L 1989 *Surf. Sci.* **211/212** 394
[6] Trott M and Schnittler C 1989 *Phys. Status Solidi* b **152** 157
[7] Economou E N 1983 *Green's Function in Quantum Physics* (Berlin: Springer) ch 3
[8] Inglesfield J E and Benesh G 1988 *Phys. Rev.* B **37** 6682
[9] Radny M 1990 *Surf. Sci.* at press
[10] Heskett D, Frank K-H, Horn K, Koch E, Freund H J, Baddorf A, Tseui K D and Plummer E W 1988 *Phys. Rev.* B **37** 10387
[11] Kubiak G 1988 *Surf. Sci.* **201** 1475