

Application of the z -transform to composite materials

Yi Qin Gao and R. A. Marcus

Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

(Received 21 May 2001; accepted 17 September 2001)

Applications of the z -transform were made earlier to interfacial electron transfer involving semi-infinite solids, e.g., semiconductor/liquid and metal/liquid interfaces and scanning tunneling microscopy. It is shown how the method is readily adapted to treat composite materials, such as solid/solid interfaces or “molecular wire”/solid interfaces. © 2001 American Institute of Physics. [DOI: 10.1063/1.1416127]

I. INTRODUCTION

The electronic structure of solids having surfaces has been of much interest in a variety of physical and chemical studies.^{1–4} Among the simple theoretical methods used for treating the electronic properties of solids the tight-binding approach is considered the simplest that is also reliable for approximate calculations.^{1,3} In the implementation of this method to solids with surfaces, the solids can be considered as consisting of coupled atomic layers parallel to the surface. The system can then be simplified as a one-dimensional chain, with each unit representing a principal layer.^{5,6} The principal layers are then treated separately using the two-dimensional space group symmetry.

Various methods have been developed in tight-binding studies of solids having surfaces. In the “slab” method⁷ the solid is treated as consisting of a finite number of principal layers parallel to the surface and the electronic structure of such a slab is usually obtained by direct diagonalization of the Hamiltonian. The elements of the Hamiltonian are expressed in terms of atomic or molecular orbitals and their interactions within and between layers. Other methods for semi-infinite solids include the transfer matrix^{6,8} and scattering-theoretic⁹ formalisms, which usually employ Green function techniques.

Instead of the Green function method, a z -transform method has also been used to treat the electronic structure of a semi-infinite solid.¹⁰ The z -transform, also known as the discrete Laplace transform,¹¹ had been applied earlier in electrical engineering and allied fields. The transform reduces the problem of solving an infinite set of linear difference equations to an algebraic equation. This transform method can be applied to multi-band and/or complex interacting systems and still be transparent in its mathematical results. It was recently used to obtain the electronic wave functions of single element (Si) and compound element (InP) semiconductors.¹² The calculated electronic wave functions were then used to calculate the electronic coupling matrix element for electron transfer reactions at semiconductor/liquid interfaces. The z -transform method proved to be efficient and the results showed good agreement with those of the slab method in those studies.

The Green function approach lends itself quite naturally

to focusing on local regions,^{13,14} such as defects or surfaces. It is adaptable to thermal averaging, and there are well-defined procedures for treating Green functions and summing over formal expansions. The wave function approach has been more commonly used in chemical studies, particularly in the form of a slab or cluster approach, since it has permitted very detailed electronic structure calculations. The Green function has been extensively used in recent years in the treatment of “molecular wires” and related systems.¹⁴

In earlier studies, the z -transform was applied to the treatment of semi-infinite solids,¹⁰ including electron transfer reactions for scanning tunneling microscopy,^{15,16} semiconductor/liquid¹² and metal/attached monolayer systems.¹⁷ In the present paper the method is extended to composite systems, such as solid/solid interfaces. The extension also applies to “molecular wire”/solid interfaces, as a particular example of a composite system. Interfaces between a metal and a semiconductor and that between two semiconductors have been studied extensively in the literature,^{18–20} and reflect the scientific and technological interest in such systems. Their electronic structures have been studied by Green function techniques, using tight-binding^{3,18} or pseudopotential methods.² In the present paper the electronic wave function of such systems is obtained by introducing separate z -transforms for the coefficients of both solids and using the interaction parameters between the two solids. Both bulk and interfacial states can be studied in this manner.

II. THE z -TRANSFORM METHOD FOR TREATING SEMI-INFINITE SOLIDS AND SOLID/SOLID INTERFACES

A. z transform

We have noted earlier the use of “principal layers,” which are parallel to the surface, and the subsequent treatment of the system is one-dimensional, each unit being a principal layer.⁵ In the following, we first consider the tight-binding wave functions for a one-dimensional solid–solid interface, and show how the z -transform method can be applied to it. For its application to solid/solid interfaces, it is useful to first illustrate the z -transform method by applying it to electronic wave functions of a semi-infinite solid. A more

detailed derivation is given in Ref. 10. In this approach the tight-binding type Hamiltonian H and electronic wave functions Ψ_k can be written as

$$H = \alpha_1 |1\rangle\langle 1| + \alpha \sum_{n=2}^{\infty} |n\rangle\langle n| + \left(\beta \sum_{n=1}^{\infty} |n+1\rangle\langle n| + \text{c.c.} \right), \quad (1)$$

$$|\Psi_k\rangle = \sum_{n=1}^{\infty} c_n(k) |n\rangle, \quad (2)$$

where $\alpha_1 = \langle 1|H|1\rangle$, $\alpha = \langle n|H|n\rangle$ (for $n \geq 2$), $\beta = \langle n+1|H|n\rangle$ (for $n \geq 1$), and the coefficient $c_n(k)$ in Eq. (2) is the solution of an infinite set of linear equations,

$$\beta^* c_{n+1} + (\alpha - E)c_n + \beta c_{n-1} = 0, \quad n \geq 2, \quad (3)$$

with the boundary condition

$$\beta^* c_2 + (\alpha_1 - E)c_1 = 0. \quad (4)$$

In the notation the k -dependence of the c_n is suppressed for brevity.

To solve the linear equations given by Eq. (3), the z -transform for c_n is defined by

$$\mathcal{Z}(c_n) = \sum_{n=1}^{\infty} c_n z^{1-n} \equiv F(z), \quad (5)$$

which, using Eqs. (3) and (4), can be shown to yield¹⁰

$$F(z) = c_1 \frac{(\alpha - \alpha_1)z + \beta^* z^2}{\beta^* z^2 + (\alpha - E)z + \beta}. \quad (6)$$

The coefficients c_n are recovered using the inverse z transform of $F(z)$,

$$c_n = \frac{1}{2\pi i} \oint_C F(z) z^{n-2} dz, \quad (7)$$

that is

$$c_n = \frac{c_1}{2\pi i} \oint_C \frac{(\alpha - \alpha_1) + \beta^* z}{\beta^* z^2 + (\alpha - E)z + \beta} z^{n-1} dz. \quad (8)$$

The latter is readily integrated using Cauchy's residue theorem. The z -transform is applied to solid/solid interfaces in the next section. For simplicity, the solid/solid interfaces will be studied using mainly one-dimensional models, but the results are immediately generalized to the 3D case. Ideal interfaces and reconstructed interfaces are treated separately in the following. The constant c_1 can be evaluated by normalizing the wave function to a delta function.¹⁰

B. Flux, transmission and reflection coefficients

In the present study we shall need expressions for the probability flux in the tight-binding approximation and for transmission and reflection coefficients at an interface. They are readily obtained: From the time-dependent Schrödinger equation $i\hbar \partial|\Psi\rangle/\partial t = H|\Psi\rangle$, and a wave function $|\Psi\rangle = \sum_m c_m(t) |m\rangle$ and operating on the left by $\langle n|$ we have

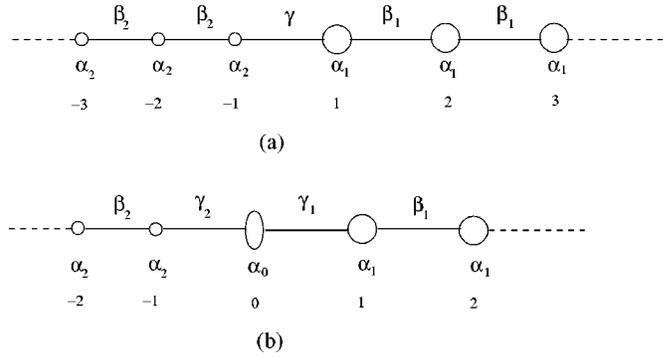


FIG. 1. Schematic picture of the interface formed by two semi-infinite linear chains: (a) an ideal interface, (b) a reconstructed (coated) interface. α , β , and γ are the interaction parameters. The sites on the left-hand side are denoted by negative numbers and the sites on the right-hand side are denoted by positive numbers.

$$i\hbar \frac{\partial c_n}{\partial t} = \langle n|H|n+1\rangle c_{n+1} + \langle n|H|n-1\rangle c_{n-1} + \langle n|H|n\rangle c_n. \quad (9)$$

Upon multiplying by c_n^* and subtracting the complex conjugate we have

$$\frac{\partial}{\partial t} |c_n|^2 = \frac{1}{i\hbar} [(\langle n-1|H|n\rangle c_{n-1}^* c_n - \text{c.c.}) - (\langle n|H|n+1\rangle c_n^* c_{n+1} - \text{c.c.})]. \quad (10)$$

The right-hand side has the form of the flux $S_{n-1 \rightarrow n}$ from site $n-1$ into site n minus the flux $S_{n \rightarrow n+1}$ out of site n into site $n+1$. We have

$$S_{n-1 \rightarrow n} = \frac{2}{\hbar} \text{Im} \langle n-1|H|n\rangle c_{n-1}^* c_n, \quad (11)$$

where Im denotes the imaginary part. In the limit where the $c_n(t)$ in Eq. (10) vary as $e^{-iEt/\hbar}$ in Eq. (10) yields the usual tight-binding equation, and the time dependence in Eq. (11) for the flux $S_{n-1 \rightarrow n}$ disappears. Equation (11) can be written in a form reminiscent of the continuum case:²¹

$$S_{n-1 \rightarrow n} = \frac{2}{\hbar} \text{Im} \beta^* c_{n-1}^* \Delta c_n, \quad (12)$$

where Δc_n is the first-order difference $c_n - c_{n-1}$.

The transmission coefficient T at the interface of two solids is given by the ratio of the transmitted and reflected fluxes

$$T = S_{\text{trans}}/S_{\text{inc}}, \quad (13)$$

while the reflection coefficient R is the ratio of reflected and incident fluxes, S_{refl} being negative

$$R = |S_{\text{refl}}|/S_{\text{inc}}. \quad (14)$$

C. Ideal interface between two one-dimensional one-band systems

The one-dimensional model of the composite interface is illustrated in Fig. 1(a). The wave function of such a system can be written in terms of localized atomic orbitals

$$|\Psi_k\rangle = \sum_{n=-\infty}^{\infty} c_n |n\rangle \quad (n \neq 0), \quad (15)$$

where $|n\rangle$ again denotes the orbital localized at the n th site.

The tight-binding Hamiltonian of this system can be written as

$$H = \sum_{n=-\infty}^{-1} \alpha_2 |n\rangle \langle n| + \left(\sum_{n=-\infty}^{-1} \beta_2 |n\rangle \langle n-1| + \text{c.c.} \right) + \sum_{n=1}^{\infty} \alpha_1 |n\rangle \langle n| + \left(\sum_{n=1}^{\infty} \beta_1 |n+1\rangle \langle n| + \text{c.c.} \right) + (\gamma |1\rangle \langle -1| + \text{c.c.}), \quad (16)$$

where β_1 and β_2 are the interaction parameters $\langle n+1|H|n\rangle$ between the neighboring sites within each of the two semi-infinite chains, denoted by positive and negative numbers, respectively, α_1 and α_2 are the corresponding Coulombic parameters, and $\gamma (= \langle 1|H|-1\rangle)$ is the interaction parameter between the two adjacent sites 1 and -1 of the two chains. As can be seen from the Hamiltonian, it is assumed here for simplicity that the interface consists of only two sites (-1 and 1), and at first the Coulombic parameter α for each of the two sites at the interface is given the same value as that in each semi-infinite solid. When the interfacial potential parameters α_1 and α_{-1} are different from their bulk values and/or when the interaction involves more than the nearest neighbors, the same derivation is applicable, but the final formulas are more complicated.

Using the same strategy as that used in the semi-infinite solid case a set of difference equations is obtained for the coefficients c_n 's, $n=1, 2, \dots, \infty$ and a set for the other coefficients, $n=-1, -2, \dots, -\infty$, instead of just one set of equations. These two sets are coupled by the coefficients c_{-1} and c_1 ,

$$\beta_1^* c_{n+1} + (\alpha_1 - E)c_n + \beta_1 c_{n-1} = 0, \quad n=2, 3, 4, \dots \quad (\text{solid 1}), \quad (17)$$

$$\beta_1^* c_2 + (\alpha_1 - E)c_1 + \gamma c_{-1} = 0, \quad (18)$$

and

$$\beta_2^* c_{n+1} + (\alpha_2 - E)c_n + \beta_2 c_{n-1} = 0, \quad n=-2, -3, -4, \dots \quad (\text{solid 2}), \quad (19)$$

$$\gamma^* c_1 + (\alpha_2 - E)c_{-1} + \beta_2 c_{-2} = 0. \quad (20)$$

The respective z transforms for solid 1 ($n \geq 1$) and solid 2 ($n \leq -1$) are

$$F^+(z) = \sum_{n=1}^{\infty} c_n z^{1-n}, F^-(z) = \sum_{n=-1}^{-\infty} c_n z^{1+n}. \quad (21)$$

With these definitions, $F^+(z)$ and $F^-(z)$ converge when $|z| \leq 1$ and $n \rightarrow \infty$ and $n \rightarrow -\infty$, respectively. Application of the z transform to the two sets of difference equations, Eqs. (17), (19), and (21) yield

$$F^+(z) = \frac{\beta_1^* z^2 c_1 + (\alpha_1 - E)z c_1 + z \beta_1^* c_2}{\beta_1^* z^2 + (\alpha_1 - E)z + \beta_1} \quad (\text{solid 1}), \quad (22)$$

$$F^-(z) = \frac{\beta_2 z^2 c_{-1} + (\alpha_2 - E)z c_{-1} + z \beta_2 c_{-2}}{\beta_2 z^2 + (\alpha_2 - E)z + \beta_2^*} \quad (\text{solid 2}). \quad (23)$$

Equations (18) and (20)–(23) yield

$$F^+(z) = \frac{c_1 \beta_1^* z^2 - c_{-1} \gamma z}{\beta_1^* z^2 + (\alpha_1 - E)z + \beta_1} \quad (\text{solid 1}), \quad (24)$$

$$F^-(z) = \frac{c_{-1} \beta_2 z^2 - c_1 \gamma^* z}{\beta_2 z^2 + (\alpha_2 - E)z + \beta_2^*} \quad (\text{solid 2}). \quad (25)$$

The coefficients obtained by the inverse z transform are

$$c_n = \frac{1}{2\pi i} \oint_C F^+(z) z^{n-2} dz \quad (\text{solid 1, } n > 0), \quad (26)$$

$$c_n = \frac{1}{2\pi i} \oint_C F^-(z) z^{-n-2} dz \quad (\text{solid 2, } n < 0). \quad (27)$$

For $n=1$ and $n=-1$, integration of Eqs. (26) and (27) yields $c_1 = c_1$ and $c_{-1} = c_{-1}$, as they should.

To obtain solutions which are propagating to infinity in both sides of the solid, c_n and c_{-n} should neither vanish nor become infinite as $n \rightarrow \infty$. (We treat bound interfacial states later.) We thus require that the poles of the integrand in Eqs. (26) and (27) lie on the unit circle, a result which implies that the solution $z = z_1$ of

$$\beta_1^* z^2 + (\alpha_1 - E)z + \beta_1 = 0 \quad (28)$$

and the solution $z = z_2$ of

$$\beta_2 z^2 + (\alpha_2 - E)z + \beta_2^* = 0 \quad (29)$$

both lie on the unit circle. In a simple case where β_1 and β_2 are real, the solutions of Eqs. (28) and (29) are both of the type $e^{\pm i\theta}$, but each typically has a different value of θ . We then have

$$E - \alpha_1 = \beta_1 (e^{i\theta} + e^{-i\theta}) = 2\beta_1 \cos \theta_1 \quad (30)$$

and

$$E - \alpha_2 = 2\beta_2 \cos \theta_2, \quad (31)$$

which also serve to relate θ_2 to θ_1 .²²

The c_n for $n > 0$, as discussed earlier, is given by Eq. (26). (The extension to complex values is readily made.) The poles of the integrand of the right-hand side of Eq. (26) occur at $z = \exp(i\theta_1)$ and $z = \exp(-i\theta_1)$. The former gives a term $\exp(in\theta_1)$ and the latter $\exp(-in\theta_1)$. After evaluating the residues, we have

$$c_n = \frac{(c_1 \beta_1 - c_{-1} \gamma e^{-i\theta_1}) e^{in\theta_1}}{2i \beta_1 \sin \theta_1} - \frac{(c_1 \beta_1 - c_{-1} \gamma e^{i\theta_1}) e^{-in\theta_1}}{2i \beta_1 \sin \theta_1} \quad (n > 0, \text{ solid 1}). \quad (32)$$

Similarly, from Eq. (27), we have

$$c_n = \frac{(c_{-1}\beta_2 - c_1\gamma e^{-i\theta_2})e^{-in\theta_2}}{2i\beta_2\sin\theta_2} - \frac{(c_{-1}\beta_2 - c_1\gamma e^{i\theta_2})e^{in\theta_2}}{2i\beta_2\sin\theta_2} \quad (n < 0, \text{ solid 2}). \quad (33)$$

The constants c_1 and c_{-1} are obtained by a normalization and by satisfying a boundary condition at infinity. For example, if a traveling wave in solid 2, $e^{in\theta_2}$, is incident from the left in Fig. 1, and is partially reflected at the interface, and a purely outgoing wave, $e^{in\theta_1}$, occurs in solid 1 then the boundary condition is to set the coefficient of the $e^{-in\theta_1}$ term ($n > 0$) in Eq. (32) equal to zero. Thereby,

$$c_1\beta_1 = c_{-1}\gamma e^{i\theta_1}, \quad (34)$$

and so from Eq. (33), denoting the c_n for the transmitted wave in solid 1 by c_n^{trans} , we have

$$c_n^{\text{trans}} = c_1 e^{i(n-1)\theta_1} \quad (n > 0). \quad (35)$$

The c_n for the incident wave part of Eq. (33) in solid 2 is denoted by c_n^{inc} and, using Eq. (34), is given by

$$c_n^{\text{inc}} = -\frac{c_1}{2i\gamma\beta_2\sin\theta_2}(\beta_1\beta_2 e^{-i\theta_1} - \gamma^2 e^{i\theta_2})e^{in\theta_2} \quad (n < 0). \quad (36)$$

The c_n for the reflected wave in solid 2 at the interface is

$$c_n^{\text{refl}} = \frac{c_1}{2i\gamma\beta_2\sin\theta_2}(\beta_1\beta_2 e^{-i\theta_1} - \gamma^2 e^{-i\theta_2})e^{-in\theta_2} \quad (n < 0). \quad (37)$$

The incident flux, using Eq. (11), is

$$S_{\text{inc}} = \frac{|c_1|^2}{4\hbar\gamma^2\beta_2\sin\theta_2}[\beta_1^2\beta_2^2 - 2\beta_1\beta_2\gamma^2\cos(\theta_1 + \theta_2) + \gamma^4]. \quad (38)$$

The reflected flux is

$$S_{\text{refl}} = -\frac{|c_1|^2}{4\hbar\gamma^2\beta_2\sin\theta_2}[\beta_1^2\beta_2^2 - 2\beta_1\beta_2\gamma^2 \times \cos(\theta_2 - \theta_1) + \gamma^4] \quad (39)$$

and the transmitted flux is

$$S_{\text{trans}} = \frac{|c_1|^2\beta_1\sin\theta_1}{\hbar}. \quad (40)$$

It is readily verified that $S_{\text{inc}} + S_{\text{refl}} = S_{\text{trans}}$, S_{refl} being negative. The ratios T and R in Eqs. (13) and (14) are immediately obtained from Eqs. (38)–(40).

Two limiting cases are readily retrieved from Eqs. (32)–(34): In the limiting case where $\gamma = 0$, the two semi-infinite solids are uncoupled, and the above expressions yield wave functions which are those of semi-infinite chains.^{1,10} The other limiting case is where the two semi-infinite chains are the same, so that $\gamma = \beta_1 = \beta_2$, $\alpha_1 = \alpha_2$, and $\theta_1 = \theta_2 = \theta$. We then have an infinite one-dimensional chain of sites, and $c_n = e^{in\theta}c_1$ for all n .

At both metal–semiconductor²³ and semiconductor–semiconductor interfaces,¹⁹ bound interfacial states are common and are known to play an important role in determining physical features such as conduction behavior¹⁸ and the Schottky barrier height.¹⁹ The bound interfacial states have been studied extensively using the Green function method.²⁴ In the following it is seen that the z -transform method similarly provides an examination of conditions and energy values for these interfacial states.

To illustrate the use of the z -transform method for this purpose, we again model such a situation by a one-dimensional chain, again taking the β 's and γ to be real, for simplicity. In this case, the solutions of Eqs. (28) and (29) are both of the form $z = e^{-\theta_{1,2}}$, where the real parts of θ_1 and θ_2 are positive. Since e^{θ_1} is also a solution of Eq. (28), in order to avoid c_n increasing as n increases, the integrand of Eq. (26) is such that the numerator has $z - e^{\theta_1}$ as a factor to cancel a corresponding term in the denominator. Thus we require that

$$c_1\beta_1 z + c_{-1}\gamma\alpha z - e^{\theta_1} \quad (41)$$

which yields

$$\frac{c_1}{c_{-1}} = -\frac{\gamma}{\beta_1} e^{-\theta_1}. \quad (42)$$

Similarly, we have that

$$\frac{c_{-1}}{c_1} = -\frac{\gamma}{\beta_2} e^{-\theta_2} \quad (43)$$

from the requirement that c_n ($n < 0$) decreases as n decreases. Comparison of Eqs. (42) and (43) finally yields

$$e^{\theta_1 + \theta_2} = \frac{\gamma^2}{\beta_1\beta_2}. \quad (44)$$

The interfacial states can exist only if Eq. (44) is satisfied, and thus $\gamma^2/\beta_1\beta_2$ must exceed unity. These results are readily extended to three-dimensional cases and complex-valued β 's and γ . The z -transform method proves to be a simple method for obtaining the existing condition of interfacial states.

D. One-dimensional one-band systems with a reconstructed and/or coated interface

When two solids form a heterojunction, the interface is frequently reconstructed. In many cases one of the solids is coated by some other material beforehand. Such systems have usually been treated by the Green function technique.²⁰ This situation is readily modeled by treating the interface as a different unit from the two bulk phases, as illustrated in Fig. 1(b). One type of atom occupies sites from 1 to ∞ , those of the other type occupy -1 to $-\infty$, and the interface occupies site 0. Using the same parameters α_1 , α_2 , β_1 , and β_2 tacitly defined in Eq. (16) and introducing

$$\alpha_0 = \langle 0|H|0\rangle, \quad \gamma_1 = \langle 1|H|0\rangle, \quad \gamma_2 = \langle 0|H|-1\rangle, \quad (45)$$

the following linear equations are obtained for this system by the same method as that described earlier,

$$\beta_1^* c_{n+1} + (\alpha_1 - E)c_n + \beta_1 c_{n-1} = 0, \quad n = 2, 3, 4, \dots, \quad (46)$$

$$\beta_1^* c_2 + (\alpha_1 - E)c_1 + \gamma_1 c_0 = 0, \quad (47)$$

and

$$\beta_2^* c_{n+1} + (\alpha_2 - E)c_n + \beta_2 c_{n-1} = 0, \quad n = -2, -3, -4, \dots, \quad (48)$$

$$\gamma_2^* c_0 + (\alpha_2 - E)c_{-1} + \beta_2 c_{-2} = 0. \quad (49)$$

Electronic wave functions of such a system can again be obtained using the z-transform method, again treating the β 's and γ as real, for simplicity. Using the boundary condition,

$$c_0 = \frac{c_1 \gamma_1 + c_{-1} \gamma_2}{E - \alpha_0}, \quad (50)$$

the tight-binding coefficients are obtained as

$$c_n = \frac{1}{2\pi i} \oint_C \frac{\left\{ c_1 \left(\beta_1 z - \frac{\gamma_1^2}{E - \alpha_0} \right) - c_{-1} \frac{\gamma_1 \gamma_2}{E - \alpha_0} \right\} z^{n-1}}{\beta_1 z^2 + (\alpha_1 - E)z + \beta_1} dz, \quad (51)$$

$$c_n = \frac{1}{2\pi i} \oint_C \frac{\left\{ c_{-1} \left(\beta_2 z - \frac{\gamma_2^2}{E - \alpha_0} \right) - c_1 \frac{\gamma_1 \gamma_2}{E - \alpha_0} \right\} z^{-(n+1)}}{\beta_2 z^2 + (\alpha_2 - E)z + \beta_2} dz. \quad (52)$$

The condition for the existence of bound interfacial states can be found in a way similar to that discussed in the preceding section. For bound interfacial states there should only be terms of exponentially decaying waves in the expression for c_n . Accordingly, terms that increase as n increases are made to vanish. As in the preceding section, one obtains

$$c_1 \left(\frac{\gamma_1^2}{E - \alpha_0} - \beta_1 e^{\theta_1} \right) = c_{-1} \frac{\gamma_1 \gamma_2}{\alpha_0 - E}, \quad (53)$$

$$c_{-1} \left(\frac{\gamma_2^2}{E - \alpha_0} - \beta_2 e^{\theta_2} \right) = c_1 \frac{\gamma_1 \gamma_2}{\alpha_0 - E}. \quad (54)$$

In order for there to be a nontrivial solution for c_1 and c_{-1} , the determinant of the coefficients in Eqs. (53) and (54) vanishes, yielding

$$\frac{\gamma_1^2}{\beta_1} e^{-\theta_1} + \frac{\gamma_2^2}{\beta_2} e^{-\theta_2} = E - \alpha_0. \quad (55)$$

The requirement that the wave functions decay in both sides of the solid yields the following condition for the existence of bound interfacial states, obtained by requiring that the poles in Eqs. (51) and (52) be of the form $z = e^{\theta_1}$ and e^{θ_2} , respectively,

$$E = \alpha_1 + 2\beta_1 \cosh \theta_1 = \alpha_2 + 2\beta_2 \cosh \theta_2, \quad \theta_1 > 0, \quad \theta_2 > 0. \quad (56)$$

It is readily verified that the expected results can be obtained for several limiting situations.

A simple semi-infinite system is achieved by setting

$$\gamma_1 = \beta_1, \quad \gamma_2 = \beta_2 = 0, \quad \alpha_2 = 0. \quad (57)$$

The condition for the existence of bound surface states can be obtained by applying the above equalities to Eqs. (55) and (56),

$$\alpha_1 - \alpha_0 = \beta_1 e^{\theta_1}, \quad \theta_1 > 0 \quad (58)$$

which can be rewritten as

$$\frac{\alpha_1 - \alpha_0}{\beta_1} > 1, \quad (59)$$

and is in agreement with the known result.^{1,10}

Another limiting case occurs when two identical semi-infinite linear chains form an interface

$$\beta_1 = \beta_2 = \gamma_1 = \gamma_2, \quad \alpha_1 = \alpha_2. \quad (60)$$

It then readily follows that the condition for the existence of bound interfacial states is

$$\alpha_1 - \alpha_0 > 0, \quad (61)$$

i.e., that the surface states below the allowed band of the infinite chain can exist only if the α_0 is more negative than α_1 .

III. CONCLUDING REMARKS

In the present study the z-transform method has been applied to composite materials, such as solid/solid interfaces. The existing condition for bound interfacial states is obtained in terms of tight-binding solid state parameters, treating both reconstructed and ideally nonreconstructed interfaces. The z transform and the models introduced in the present paper can be applied to systems of experimental interest, including charge transfer through diodes and molecular wires. In particular, it can be applied, using the tight-binding wave functions, to study the interface between a "molecular wire" and a metallic surface²⁵ and the contact between nanotubes and metals.²⁶

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the support of this research by the National Science Foundation and the Office of Naval Research.

¹S. G. Davison and M. Steslicka, *Basic Theory of Surface States* (Clarendon, Oxford, 1996).

²F. Garcia-Moliner and V. R. Velasco, *Theory of Single and Multiple Interfaces* (World Scientific, Singapore, 1992).

³F. Bechstedt and R. Enderlein, *Semiconductor Surfaces and Interfaces* (Akademie-Verlag, Berlin, 1988).

⁴M. Lannoo and P. Friedel, *Atomic and Electronic Structure of Surfaces* (Springer-Verlag, Berlin, Heidelberg, 1991).

⁵For example, Ref. 3, pp. 131–133.

⁶D. H. Lee and D. Joannopoulos, *Phys. Rev. B* **23**, 4988 (1981).

⁷For example, K. Hirabayashi, *J. Phys. Soc. Jpn.* **27**, 1475 (1969); C. Calandra, F. Manghi, and C. M. Bertoni, *J. Phys. C* **10**, 1911 (1977); D. J. Chadi, *Phys. Rev. B* **18**, 1800 (1978); K. C. Pandey and J. C. Philips, *Phys. Rev. Lett.* **34**, 1450 (1975).

⁸E. J. Mele and J. D. Joannopoulos, *Phys. Rev. B* **17**, 1816 (1978).

⁹For example, J. Koutecky and M. Tomasek, *Phys. Rev.* **120**, 1212 (1960); I. Ivanov and J. Pollmann, *Solid State Commun.* **36**, 361 (1980). A scattering formalism for STM and related "molecular wire" problems has been used in M. Magoga and C. Joachim, *Phys. Rev. B* **56**, 4722 (1997) and in references to P. Sautet and C. Joachim cited therein; also E. G. Emberly and G. Kirczenow, *ibid.* **58**, 10911 (1998).

¹⁰R. A. Marcus, *J. Chem. Phys.* **98**, 5604 (1993).

- ¹¹For example, J. R. Ragazzi and L. A. Zadeh, *Trans. Am. Inst. Electr. Eng.* **71**, 225 (1952); E. I. Jury, *ibid.* **73**, 332 (1954).
- ¹²Y. Q. Gao, Y. Georgievskii, and R. A. Marcus, *J. Chem. Phys.* **112**, 3358 (2000).
- ¹³Extensive references to the use of Green function methods are given in Ref. 1, Chap. 7, as well as in J. E. Inglesfield, *Prog. Surf. Sci.* **25**, 57 (1978) and in J. Pollman and S. T. Pantelides, *Phys. Rev. B* **18**, 5524 (1978), papers which describe advantages of a Green function approach.
- ¹⁴For example, S. N. Yaliraki, M. Kemp, and M. A. Ratner, *J. Am. Chem. Soc.* **121**, 3428 (1999) and references cited therein; S. Datta, W. Tian, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, *Phys. Rev. Lett.* **79**, 2530 (1997) and references cited therein; C. P. Hsu and R. A. Marcus, *J. Chem. Phys.* **106**, 584 (1997); L. E. Hall, J. F. Reimers, N. S. Hush, and K. Silverbrook, *ibid.* **112**, 1510 (2000).
- ¹⁵H. Ouyang and R. A. Marcus, *J. Chem. Phys.* **100**, 7814 (1994).
- ¹⁶STM has been treated as a solid–molecule–solid system using a tight-binding model, C. Joachim and P. Sautet, in *STM and Related Methods*, R. J. Behm, N. Garcia, and H. Rohrer, NATO ASI ser., Ser. E **184**, 377 (1990).
- ¹⁷S. Gosavi and R. A. Marcus, *J. Phys. Chem. B* **104**, 2067 (2000).
- ¹⁸For example, S. G. Davison and J. D. Levine, *Solid State Phys.* **25**, 1 (1970); D. J. Chadi and M. L. Cohen, *Phys. Status Solidi B* **68**, 405 (1975); Y. R. Yang and C. B. Duke, *Phys. Rev. B* **36**, 2763 (1987).
- ¹⁹For example, W. Schottky, *Z. Phys.* **113**, 367 (1939); A. Zur, T. C. McGill, and D. L. Smith, *Phys. Rev. B* **28**, 2060 (1983); E. J. Mele and J. D. Joannopolous, *ibid.* **17**, 1528 (1978); J. Tersoff, *Phys. Rev. Lett.* **52**, 465 (1984); *Phys. Rev. B* **30**, 4874 (1984).
- ²⁰For example, W. Moench, *J. Vac. Sci. Technol. B* **14**, 2985 (1996); A. K. Agrawal, *Phys. Rev. B* **23**, 2995 (1981); D. N. Lowy and A. Madhukar *ibid.* **17**, 3832 (1978).
- ²¹In the continuum case we have instead $S = (\hbar/\mu)\text{Im} \Psi^* \partial\Psi/\partial x$. If a denotes the length of a unit cell, and if Ψ is locally normalized to a cell of length a , the counterpart of the β in Eq. (12) is $\hbar^2/2\mu a$.
- ²²When β_1 and β_2 are not real, Eqs. (32) and (33) again follow, but with the β 's replaced by $|\beta|$'s and the θ 's each having an additional phase angle.
- ²³V. Heine, *Phys. Rev.* **A138**, 1689 (1965).
- ²⁴For example, N. V. Dandekar, A. Madhukar, and D. N. Lowry, *Phys. Rev. B* **21**, 5687 (1980); B. Djafari-Rouhani, L. Dobraynski, and M. Lannoo, *Surf. Sci.* **78**, 24 (1978); R. N. Nucho and A. Madhukar, *J. Vac. Sci. Technol.* **15**, 1530 (1978).
- ²⁵S. N. Yaliraki, A. E. Roitberg, C. Gonzalez, V. Mujica, and M. A. Ratner, *J. Chem. Phys.* **111**, 6997 (1999); S. N. Yaliraki and M. A. Ratner, *ibid.* **109**, 5036 (1998).
- ²⁶M. P. Anantram, S. Datta, and Y. Xue, *Phys. Rev. B* **61**, 14219 (2000).