Tight-binding approximation for semi-infinite solids. Application of a transform method and of delta function normalization

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A transform method for treating semi-infinite solids in the tight-binding (TB) approximation is introduced. The difference equations for the TB orbital coefficients are converted, thereby, to convenient algebraic equations. For this purpose, a Dirac delta function normalization for the wave function is also introduced, instead of the usual box one. Single and coupled bands are treated, and the methods are applied elsewhere to electron transfer problems at interfaces.

I. INTRODUCTION

The dependence of long-range electron (or hole) transfer (ET) rates on the separation distance and on the intervening molecular material is the subject of much current experimental interest. Rigid organic structures, proteins, and frozen media have all been used as bridges between the electron donor (D) and acceptor (A). For interpreting the experiments on these nonadiabatic processes, theoretical calculations of the electronic coupling, particularly their relative values, are helpful. In extended Hückel (EH) calculations made for the first two types of bridges, we found encouraging agreement with the experimental data for the relative values of the coupling. No adjustable parameters were used,[1] the EH parameters having been obtained from other (nonelectron transfer) sources.

Another set of experiments involves, instead, ET between a solid and the D or A. Examples include ET between a metal electrode and a D or A, separated from the metal by an ordered layer of long-chain adsorbed molecules. This D or A is in solution, but is either chemically bound to one end of the long chain[2] or, in a different study, moves freely in the solution.[3] Other examples include ET between semiconductors and a D or A in solution. Scanning tunneling microscopy of adsorbates or of the bare electrode provides yet another, the D or A now being a metal tip. The present paper is written with applications to these different problems in mind.

The tight-binding (TB) method has been widely used in treating the electronic properties of solids and of their surfaces, e.g., see Refs. 4–15. Typically, it has been used in a semiempirical manner, its advantage being one of simplicity. For our purpose, it is easily combined with the EH treatment used in our earlier work on long-range ET in molecules or proteins. Both treatments are L.C.A.O. in nature and are, in fact, equivalent when corresponding approximations are employed.

Although initially developed in 1928 by Bloch[9] and applied to surfaces by Goodwin[10] in 1939, the extensive use of the TB approximation continued into more recent times, e.g., Refs. 4–15. In the implementation of the approximation to solids with surfaces, the surface layer and each parallel underlying layer have often been treated separately, utilizing any two-dimensional space group symmetry. The coupling of the layers is then introduced and yields a one-dimensional chain where each unit in the chain represents an entire layer, or sometimes represents a superlayer which is composed of several actual layers to satisfy a repeat property of the solid.[11]

Various methods have been devised for implementing the TB approximation for solids with a surface. They include "slab" methods, in which a finite number of layers of the solid parallel to the surface are treated,[4,5] frequently by direct diagonalization of the resulting Hamiltonian matrix. Semi-infinite methods have also been used, involving a transfer matrix,[4,6] or a scattering-theoretic[4,7] or other formalisms.[8] For the semi-infinite treatments, Green function techniques have usually been employed.

We have made use of the slab method elsewhere,[16] but an aim of the present paper is to develop for the solid-adsorbate system a simple semi-infinite method which can be immediately combined with the EH orbital method used for electron (hole) transfer in molecules in earlier work in this series.[1] For this purpose a method is formulated in this paper utilizing the so-called z transform. The z transform[17–20] was introduced and so named[18,19] in the early 1950's as a method of treating sampled-data systems (a method relating the output to the input in such systems). It is the discrete analog of the Laplace transform, and so, we find, is well suited to the present problem of solving linear difference equations with initial conditions, for the coefficients in the wave function. In the present case these conditions are the boundary conditions at the surface. An advantage of the transform method is that it provides a systematic and simple way of reducing the problem of solving the difference equations to one of algebra, even for the case where there are a number of interacting bands with complex-valued coefficients.

The z-transform method has been applied in the electrical engineering and allied fields.[17–20] While it does not appear to have been used for the TB problem heretofore, the method was early recognized[18] as being equivalent to the generating function method employed[21] for *solving linear* difference equations. A generating function method

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has, indeed, been used by Hoffmann[12] in 1951–52 for solving recursive equations for TB secular determinants. Upon obtaining the eigenvalues, he then calculated the coefficients of the atomic orbitals in the eigenfunctions. Instead, we use what appears to be, upon comparing with the presentation in Ref. 12, a simpler approach: We apply the z transform (or generating function) directly to the difference equations for the coefficients themselves. (Other, more minor, differences from the work in Ref. 12, are in the method used for inversion—we use the residue theorem—and in the normalization, the Hoffman normalization being to a "box" of sites in the crystal.)

Several forms of normalization of TB wave functions have been employed in the literature. For example, in the case of the bulk solids, some studies employ no explicit normalization,[13] while others use normalization to a box consisting of a finite number of atoms N.[14] The latter is also used in the slab/diagonalization treatment of the surface properties. The Born–von Karman periodic boundary condition,[15] using a finite number of atoms, has also been used. In our case, since the orbitals of a semi-infinite system are being calculated, we have introduced a Dirac delta function normalization. While this normalization has been widely used in gas phase collision problems, and has been referred to in a bulk normalization,[14b] I am unaware of its having been applied to surface TB problems. Nevertheless, its use in the present surface problem permits us to utilize in a simple way the z-transform method. Of course, the final results for any observable would be the same, in the limit of $N\to\infty$, regardless of which method is used.

The organization of the paper is as follows: The layer description for treatment of surfaces[22] and the present normalization are both discussed in Sec. II. The z-transform or generating function method is given in Sec. III. It is applied to single band systems with complex coefficients in Sec. IV, to bound surface states in Sec. V, and to multiband systems with complex coefficients in Sec. VI. The "counting" of states for the delta function normalization is discussed in Sec. VII.

II. LAYER DESCRIPTION AND DELTA FUNCTION NORMALIZATION

A. Normalization for an infinite system

For introduction in the Schrödinger equation

$$H\Psi=E\Psi \tag{2.1}$$

the TB wave function for a one-band one-dimensional infinite chain is written as

$$\Psi=\sum_{n=-N}^{N} c_n\Phi_n \quad (N\to\infty), \tag{2.2}$$

where Φ_n is a wave function localized on the nth site. In the case of coupling only between adjacent sites, we have, on multiplying Eq. (2.1) by Φ_n^*, introducing Eq. (2.2), and integrating,

$$\beta^*c_{n+1}+(\alpha-E)c_n+\beta c_{n-1}=0 \quad (-\infty<n<\infty), \tag{2.3}$$

where

$$\alpha=H_{nn}=\langle\Phi_n|H|\Phi_n\rangle, \tag{2.4}$$

$$\beta=H_{n+1,n}=\langle\Phi_{n+1}|H|\Phi_n\rangle. \tag{2.5}$$

Introduction of next-nearest couplings or of higher order couplings leads thereby to a higher order difference equation. If, as a solution to Eq. (2.3), the term γ^n is introduced for c_n, one obtains

$$\beta^*\gamma^2+(\alpha-E)\gamma+\beta=0. \tag{2.6}$$

In order that all c_n be bounded and nonzero as $n\to\infty$, we require that γ lie on the unit circle in the complex plane. Thereby, γ equals $\exp(i\Phi)$, where Φ is real. To simplify the subsequent notation, we write, in anticipation,

$$\gamma=e^{-i\delta}e^{i\theta}, \tag{2.7}$$

where θ can be positive or negative, and where $-\delta$ is the phase of β,

$$\beta=|\beta|e^{-i\delta}. \tag{2.8}$$

When the orbitals Φ_n in Eq. (2.2) are real, δ is zero. Equations (2.6)–(2.8) yield

$$E-\alpha=2|\beta|\cos\theta. \tag{2.9}$$

Since E and α are real, θ is also real, and so there is consistency, i.e., there is a solution of Eq. (2.6) on the unit circle.

The solutions (2.2) are thus

$$\Psi=c\sum_{-\infty}^{\infty}\mathrm{e}^{in(\theta-\delta)}\Phi_n. \tag{2.10}$$

We see from Eqs. (2.9) and (2.10) that θ lies in the interval $(-\pi,\pi)$, no independent solutions being generated when θ lies outside this range. Sometimes, instead of θ, another dimensionless quantity $k(=\theta/2\pi)$ appears in such Bloch sums, where k lies in a unit interval.[23] We shall use the latter form in applications. Also, a new θ, equal to the old one minus δ, could be introduced into Eq. (2.10), so that θ instead of $\theta-\delta$ would appear there. However, the argument in the cosine in Eq. (2.9) would then be changed to $\theta+\delta$.

The normalization of Ψ we shall use is based on the relation[24]

$$\sum_{-\infty}^{\infty}\mathrm{e}^{2\pi inx}=\delta(x). \tag{2.11}$$

Actually the right-hand side consists of an infinite sum of delta functions (cf. the Appendix), but only the one indicated in Eq. (2.11) lies in the interval $(-\pi,\pi)$ being considered.

We consider two Ψ's of different energies E and E', and hence, by Eq. (2.9), different θ's. We have, from Eqs. (2.10) and (2.11), using the $2\Pi k$ instead of the θ notation,

$$\int_{-\infty}^{\infty}\Psi'^*\Psi\,dx=c^2\sum_{-\infty}^{\infty}e^{2\pi in(k-k')}=c^2\delta(k-k'). \tag{2.12}$$

Thus $c=1$. [The δ in Eq. (2.10) is the same for Ψ and for Ψ', since it depends on β and not on E.] If overlap integrals had not been neglected, we would have obtained, instead of Eq. (2.12),

$$\int_{-\infty}^{\infty} \Psi'^{*}\Psi\, dx = c^2[1+2|S|\cos(2\pi k-\zeta)]\delta(k-k'), \tag{2.13}$$

where ζ is $\delta+\xi$, ξ being the phase of the overlap integral $S=\int \Phi_{n+1}^{*}\Phi_n\, dx = |S|\exp(i\xi)$. The constant c is then modified from its previous value accordingly.

B. Layers

A two-dimensional wave function is treated analogously, the detailed expressions depending on the topology of the lattice. We use a description based on one widely used, e.g., Ref. 22. In a two-dimensional lattice parallel to the surface plane, the unit cells extend from $-\infty$ to $+\infty$ in the two dimensions, while in a direction inward from the surface plane (along some unit cell axis, for example), they extend from 1 to ∞. The components k_1 and k_2 of wave vector $\mathbf{k}_\parallel$ in the (two-dimensional) layer are good quantum numbers, because of the translational symmetry. The position of a surface unit cell in the two-dimensional lattice (i.e., in a layer) is denoted by the vector $\mathbf{r}$, while a vector from the surface plane to the mth atomic layer is denoted by $\mathbf{t}_{m\perp}$. The position of an atom of type p in the mth atomic layer in a surface unit cell is denoted by the vector $\mathbf{t}_{m\parallel}^{p}$. (When the surface and other layers are identical, $\mathbf{t}_{m\parallel}^{p}$ is independent of m.) Thereby, the position of this mpth atom in the crystal is denoted by $\mathbf{r}+\mathbf{t}_{m\parallel}^{p}+\mathbf{t}_{m\perp}$. The orbitals $\Phi_{\mathbf{k}_\parallel}^{amp}$ of the mth layer, for a given atomic orbital a of the atoms p, are Bloch sums

$$\Phi_{\mathbf{k}_\parallel}^{amp}(\mathbf{r}_e) = c\sum_{r} e^{i\mathbf{k}_\parallel\cdot(\mathbf{r}_e-\mathbf{r}-\mathbf{t}_{m\parallel}^{p}-\mathbf{t}_{m\perp}-\Delta_r)} \times\Phi_a(\mathbf{r}_e-\mathbf{r}-\mathbf{t}_{m\parallel}^{p}-\mathbf{t}_{m\perp}), \tag{2.14}$$

where Δ_r is some two-dimensional vector analog of the phase δ which appeared in Eq. (2.8) and is absent when real atomic orbitals are used, and $\mathbf{r}_e$ denotes the coordinates of the electron. The sum over $\mathbf{r}$ in Eq. (2.14) is over all unit cells in the mth layer.

A group of successive atomic layers can, from a labeling point of view, be grouped together to form the minimal periodic unit, a "superlayer," and given a principal label n. Thereby, each layer or superlayer n is associated with a number of bands, each defined by its *amp* $\mathbf{k}_\parallel$ label.[11] The normalization of the three-dimensional wave function Ψ is expressed in terms of the three components, k_1, k_2, and k_3, of the wave vector, labeled by k

$$\langle\Psi'|\Psi\rangle=\delta(k_1-k_1')\delta(k_2-k_2')\delta(k_3-k_3'). \tag{2.15}$$

We shall introduce a notation

$$\delta(\mathbf{k}_\parallel-\mathbf{k}_\parallel') \equiv \delta(k_1-k_1')\delta(k_2-k_2'). \tag{2.16}$$

A single-band system is considered next and then extended to multiband systems in Sec. VI. Throughout we use a surface unit cell large enough (when necessary) that the first layer has the same translational symmetry for the unit cells as the underlying layers, and focus our attention on such commensurate systems.

C. Semi-infinite system and normalization

We consider next a semi-infinite system consisting of a one-dimensional chain. Each unit in the chain consists of a superlayer or layer orbital described in the previous section. We consider the case where there is only one layer in each superlayer, but the argument is easily extended. The multiband analysis in Sec. VI serves as such an extension.

Into the Schrödinger equation [Eq. (2.1)] we introduce the TB wave function for a semi-infinite solid

$$\Psi=\sum_{1}^{N} c_n\Phi_n \quad (N\to\infty), \tag{2.17}$$

where Φ_n is the wave function for the orbital for the nth layer [given by Eq. (2.14) with $m=n$ in the case of one layer in a superlayer]. Because of the translational symmetry, Φ_n is a running wave with k_1 and k_2 as good "quantum numbers." The case of coupling only between adjacent layers is considered, but as noted earlier, can be generalized. We multiply Eq. (2.1) by $\Phi_n'^{*}$, where Φ_n' differs from Φ_n only in having k_1' and k_2' as the values of the quantum numbers, instead of k_1 and k_2. Upon using Eq. (2.17), integrating over all space, and neglecting overlap integrals, we then have

$$\beta^{*}c_{n+1}+(\alpha-E)c_n+\beta c_{n-1}=0, \tag{2.18a}$$

$$\beta^{*}c_3+(\alpha-E)c_2+\beta_1 c_1=0, \tag{2.18b}$$

$$\beta_1^{*}c_2+(\alpha_1-E)c_1=0, \tag{2.18c}$$

where

$$\langle\Phi_n'|H|\Phi_n\rangle=H_{nn}=\alpha\delta(\mathbf{k}_\parallel-\mathbf{k}_\parallel'), \tag{2.19a}$$

$$\langle\Phi_{n+1}'|H|\Phi_n\rangle=H_{n+1,n}=\beta\delta(\mathbf{k}_\parallel-\mathbf{k}_\parallel'), \tag{2.19b}$$

$$H_{11}=\alpha_1\delta(\mathbf{k}_\parallel-\mathbf{k}_\parallel'), \quad H_{21}=\beta_1\delta(\mathbf{k}_\parallel-\mathbf{k}_\parallel'), \tag{2.19c}$$

and the notation $\delta(\mathbf{k}_\parallel-\mathbf{k}_\parallel')$, defined in Eq. (2.16), is used. The α, β, α_1, and β_1 are defined by the second equalities in Eqs. (2.19). The β and β_1 are sometimes complex valued.[25]

The surface layer itself may be the adsorbate layer and so have a Coulombic matrix element, α_1, and an exchange matrix element connecting to the first layer of the underlying solid, β_1, which differ from those of the bulk solid, α and β. Even in the case where there is no adsorbate, the α of the surface layer, α_1, may differ somewhat from that of the inner layers, and provide, thereby, the basis for a Tamm type of bound surface state.[10]

To consider the normalization in a general way at first, we introduce the equations for the coefficients when the energy is E', denote the coefficients by primes, and take the complex conjugate of the resulting equations,

$$\beta c_{n+1}'^{*}+(\alpha-E')c_n'^{*}+\beta^{*}c_{n-1}'^{*}=0, \tag{2.20a}$$

$$\beta c_3'^* + (\alpha - E')c_2'^* + \beta_1^* c_1'^* = 0, \tag{2.20b}$$

$$\beta_1 c_2'^* + (\alpha_1 - E)c_1'^* = 0. \tag{2.20c}$$

Multiplying Eq. (2.18a) by $c_n'^*$, Eq. (2.20a) by c_n, subtracting, and summing over n from 1 to N, we have

$$c_{N+1}(\beta c_N')^* - c_{N+1}'^* \beta c_N + \sum_1^N c_N c_N'^* (E' - E) = 0. \tag{2.21}$$

We recall next that the wave function (2.17) for this semi-infinite system yields

$$\langle \Psi' | \Psi' \rangle = \left(\lim_{N\to\infty} \sum_1^N c_N'^* c_N \right) \delta(\mathbf{k}_\parallel - \mathbf{k}_\parallel'), \tag{2.22}$$

since $\langle \Phi_n' | \Phi_n \rangle$ contributes $\delta(\mathbf{k}_\parallel - k_\parallel')$ to the normalization.

When E lies within a band, the solution of Eqs. (2.18a)–(2.18c) for a single-band system is a standing wave

$$c_n = A e^{-i(n-2)\delta} \sin[(n-1)\theta + \eta], \quad (0 < \theta < \pi), \tag{2.23}$$

as will be seen later, where $-\delta$ is the phase of the β defined by Eq. (2.8), but now β denotes a layer–layer interaction. The amplitude A and the phase η in Eq. (2.23) are both functions of θ, and the dependence of c_n on θ is seen later to be such that c_n is unchanged when θ is replaced by $-\theta$. The energy depends on $\cos\theta$, as in Eq. (4.6) below. Thereby, θ now lies in the interval $(0,\pi)$, since no new solution occurs when θ is negative. Also, this θ is now the θ for the one-dimensional chain of layers below. Thereby, θ now lies in the interval $(0,\pi)$, since no new solution occurs when θ is negative. Also, this θ is now the θ for the one-dimensional chain of layers.

We thus have from Eqs. (2.21) and (2.23), after minor manipulation,

$$\sum_1^N c_N c_N'^* = AA'^* \Big\{ \sin\Big(N - \frac{1}{2}\Big)[(\theta - \theta') + (\eta - \eta')/(N - \tfrac{1}{2})] \sin\Big(\frac{\theta + \theta'}{2}\Big) + \sin(N - \tfrac{1}{2})[(\theta + \theta') + (\eta + \eta')/(N - \tfrac{1}{2})] \times \sin\Big(\frac{\theta - \theta'}{2}\Big) \Big\} \Big/ (E' - E). \tag{2.24}$$

The highly oscillating function of $(N-\frac{1}{2})(\theta+\theta')$, which would give rise to a $\delta(\theta+\theta')$, makes no contribution, since we do not have $\theta = -\theta'$ in the interval $(0,\Pi)$. We may ignore that term and so obtain, on introducing the notation $\theta = 2\pi k_3$, with $(0 < k_3 < 1/2)$,

$$\lim_{N\to\infty} \sum_1^N c_N c_N'^* = (|A|^2/4|\beta|)\delta(k_3 - k_3'), \tag{2.25}$$

upon again using the relation $\delta(x) = (dy/dx)_0 \delta(y)$, where $y = E - E'$, $x = k_3 - k_3'$, and the 0 subscript denotes the value at $x = 0$, the relation between E and θ being given by Eq. (4.6) below. A common representation of $\delta(x)$, $\lim \sin Nx/\pi x$ as $N \to \infty$, is also used.

To solve the series of equations, Eqs. (2.20), and obtain the results used above, one method would be to set $c_n = \gamma^n$ and solve for γ. However, γ merely prescribes how each successive c_n in a series is related to the preceding one, but does not in itself prescribe the starting point of a series or how many series are needed, as a linear combination, to satisfy the boundary conditions (2.20b) and (2.20c). For example, it will be seen in Sec. V that the solution (2.23) for c_n is actually a linear combination of the six terms $\exp(\pm in\theta)$, $\exp[\pm i(n-1)\theta]$, and $\exp[\pm i(n+1)\theta]$. The transform method, applied in Sec. IV, provides a convenient and more systematic method for solving Eqs. (2.20), as well as for solving the more complicated equations that exist in multiband systems, in the same way that the Laplace transform does for analogous linear differential equations.

Equation (2.21) is, incidentally, a discrete analog of the expression sometimes used to show normalization to a Dirac delta function for collision systems: In a three-dimensional collision problem (with or without additional internal coordinates of the colliding species), it will be recalled, one again obtains a difference of two Schrödinger expressions $\Psi'^* H\Psi - \Psi H\Psi'^*$ and integrates, leaving an integral over the radial motion $r(0 < r < R)$, where ultimately $R \to \infty$. Cancellation and integration over r in the interval $(0,R)$ yields the continuous analog of Eq. (2.21) and, thereby, a Dirac delta function. In fact, this continuous analog prompted the present argument leading to Eq. (2.21).

III. z TRANSFORMATION

The z-transform method, as noted earlier, has been used for difference equations arising in another area.[17–20] The transform $F(z)$ is defined by

$$F(z) = \sum_{n=1}^{\infty} c_n z^{1-n} \equiv G c_n, \tag{3.1}$$

where the operator G is defined by the second equality in Eq. (3.1). The Laurent series (3.1) converges for $|z|$ greater than some value. The inversion formula is given by

$$c_n = \frac{1}{2\pi i} \oint_C F(z) z^{n-2}\, dz, \tag{3.2}$$

where C is a contour large enough that the integrand is analytic outside it. The application of the operator G to c_{n+1} and c_{n+2} yields

$$G c_{n+1} = zF(z) - zc_1, \tag{3.3}$$

$$G c_{n+2} = z^2 F(z) - z^2 c_1 - z c_2. \tag{3.4}$$

We apply this transform to Eqs. (2.18) in Secs. IV and V, and to equations for more complicated systems in Sec. VI. If, instead of $1/z$ in Eq. (3.1), one had used z, the resulting $F(1/z)$ would have been the usual generating function.

IV. SINGLE BAND WITH COMPLEX COEFFICIENTS

When Eqs. (3.1) and (3.3)–(3.4) are applied to Eqs. (2.18a) and (2.18b), we find

$$F(z)=c_1+\frac{-\beta_1 c_1+\beta^* z c_2}{\beta^* z^2+(\alpha-E)z+\beta}. \tag{4.1}$$

Introduction of the boundary condition (2.18c) then yields

$$F(z)=c_1-\frac{\beta_1+(\alpha_1-E)(\beta^*/\beta_1^*)z}{\beta^* z^2+(\alpha-E)z+\beta}c_1, \tag{4.2}$$

and, from Eq. (3.2) we then have

$$c_n=c_1\delta_{n1}-\frac{1}{2\Pi i}\oint_C \frac{\beta_1+(\alpha_1-E)(\beta^*/\beta_1^*)z}{\beta^* z^2+(\alpha-E)z+\beta} z^{n-2}\,dz. \tag{4.3}$$

An examination of the integral for $n=1$ shows that it makes no contribution to c_n (a simple proof involves a transformation to $w=1/z$),[26] and so Eq. (4.3) yields $c_1=c_1$, as it should. For $n\neq 1$, however, only that integral contributes to c_n. The poles in the integrand in Eq. (4.3) for $n\neq 1$ satisfy

$$\beta^* z^2+(\alpha-E)z+\beta=0, \tag{4.4}$$

whose solutions are denoted below by z_1 and z_2.

To have solutions for c_n which do not vanish or become infinite as $n\to\infty$, we require, as is seen from Eq. (4.3) and Cauchy's residue theorem, that $|z_1|$ and $|z_2|$ be unity, i.e., that these two poles lie on the unit circle in the complex plane. Thereby, the roots z_1 and z_2 can be written as

$$z_1,z_2=e^{-i\delta}e^{\pm i\theta}, \tag{4.5}$$

using a form which simplifies the subsequent notation, and θ again denotes $2\pi k_3$. The $-\delta$ in Eq. (4.5) is the phase of β, as in Eq. (2.8). One then sees from Eqs. (4.4) and (4.5) that θ satisfies

$$E-\alpha=2|\beta|\cos\theta. \tag{4.6}$$

Since E and α are real, this θ is indeed real, and so there is again internal consistency.

Equation (4.3) then yields, for $n>1$,

$$c_n=-\frac{c_1 e^{-i(n-2)\delta}}{|\beta|\beta_1^*\sin\theta}[(|\beta_1|^2-|\beta|^2)\sin(n-2)\theta + (\alpha_1-\alpha)|\beta|\sin(n-1)\theta-|\beta|^2\sin n\theta], \quad n>1. \tag{4.7}$$

This expression for c_n takes on a very simple form only when $|\beta_1|=|\beta|$ and $\alpha_1=\alpha$.

Using Eqs. (A3)–(A5), the Ψ given by Eqs. (2.17) and (4.7) satisfies the delta function normalization to the energy, $\delta(E-E')$, with c_1 given by

$$c_1=\left(\frac{\omega\sin\theta}{\pi|\beta|}\right)^{1/2}[\omega^2+4(1-\omega)\omega^2\cos^2\theta+\gamma^2 +2\gamma(\omega-2)\cos\theta]^{-1/2}, \tag{4.8}$$

where ω and γ are now defined by

$$\omega=|\beta_1|^2/|\beta|^2, \quad \gamma=(\alpha_1-\alpha)/|\beta|. \tag{4.9}$$

V. BOUND SURFACE STATES

We turn next to the question of bound surface states for a one-band system. The c_n's for a surface state tend, by definition, to zero when $n\to\infty$. We require, thereby, that any poles in the integrand in Eq. (4.3) lie *within*, rather than on or outside, the unit circle in the complex z plane. To this end, we can set in Eq. (4.4)

$$z_1,z_2=\pm e^{-i\delta}e^{-\theta}, \tag{5.1}$$

where the real part of θ is positive, and where we have introduced the $-\delta$, as before, to simplify the subsequent notation. Equation (4.4) then yields

$$E-\alpha=\pm 2|\beta|\cosh\theta, \tag{5.2}$$

so that θ is seen to be purely real, since E and α are real. The sign in Eq. (5.2) is positive or negative according as the sign in Eq. (5.1) is positive or negative, respectively. Since $\cosh\theta>|\cos\theta|$, the surface state thus lies at an energy E below or above the band (4.6), according as the negative or positive sign in Eq. (5.1) is used.

We consider first the $E<E_{\text{band}}$ case, that is, the negative sign in Eqs. (5.1) and (5.2). We now introduce the condition that there be no pole at $z=-\exp(-i\delta+\theta)$, so as to avoid the c_n's growing with n instead of decreasing. This goal can be accomplished by choosing E in the numerator of Eq. (4.3), so that the numerator has $[z+\exp(-i\delta+\theta)]$ as a factor, thus cancelling the corresponding factor in the denominator. Thus we require that

$$\beta_1+(\alpha_1-E)(\beta^*/\beta_1^*)z\propto(z+e^{-i\delta}e^{\theta}). \tag{5.3}$$

Using Eq. (5.2) with the negative sign, it follows that

$$\beta_1+(\alpha_1-\alpha+2|\beta|\cosh\theta)(\beta^*/\beta_1^*)z\propto(z+e^{-i\delta}e^{\theta}), \tag{5.4}$$

and so

$$\frac{\omega}{(2\cosh\theta)+\gamma}=e^{\theta}, \tag{5.5}$$

where ω and γ are defined by Eq. (4.10).

Equation (5.5) provides the condition for a bound surface state below the energy band. This equation imposes a condition on θ, and hence, via Eq. (5.2), on the energy E for the existence of a surface state. When $|\beta_1|=|\beta|$, it is seen from Eq. (5.5) that

$$\exp\theta=(\alpha-\alpha_1)/|\beta|, \quad (|\beta_1|=|\beta|), \tag{5.6}$$

a result found earlier using a finite size crystal.[10] Since $\theta>0$, Eq. (5.6) shows that the surface state then exists at an energy below the band [the negative sign in Eq. (5.2)] only when α_1 is more negative than α.

We consider next the case of a surface state with an energy above the band [the positive sign in Eq. (5.2)]. The poles are now given by Eq. (5.1) with the *positive sign and* one finds that Eq. (5.5) is replaced by

$$\frac{\omega}{(2\cosh\theta)-\gamma}=e^{\theta}. \tag{5.7}$$

Accordingly, in the case of $|\beta_1|/|\beta|=1$, Eq. (5.7) takes on a simpler form

$$\exp\theta=(\alpha_1-\alpha)/|\beta|, \quad (|\beta_1|=|\beta|). \tag{5.8}$$

Since θ is positive, the surface state at an energy E above the band then occurs only when α_1 is less negative than α.

VI. MULTICOUPLED BANDS WITH COMPLEX COEFFICIENTS

We consider next M coupled bands. They can arise when each atom in a layer has a number of orbitals, or when each unit in the chain of layers is the superlayer discussed earlier, or both. The wave function for this system can be written as

$$\Psi=\sum_{i=1}^{M}\sum_{n=1}^{\infty}c_{in}\Phi_{in} \tag{6.1}$$

where Φ_{in} denotes the wave function for the ith zeroth order band in layer n. The difference equations are now

$$\beta_{ii}^{*}c_{i,n+1}+(\alpha_{ii}-E)c_{in}+\beta_{ii}c_{i,n-1}+\sum_{j\neq i}(\gamma_{ij}^{*}c_{j,n+1}+\alpha_{ij}c_{jn}+\beta_{ij}c_{j,n-1})=0 \quad (n>1) \tag{6.2a}$$

and

$$\beta_{ii}^{*}c_{i3}+(\alpha_{ii}-E)c_{i2}+\beta_{ii}^{1}c_{i1}+\sum_{j\neq i}(\gamma_{ij}^{*}c_{j3}+\alpha_{ij}c_{j2}+\beta_{ij}^{1}c_{j1})=0, \tag{6.2b}$$

$$\beta_{ii}^{1*}c_{i2}+(\alpha_{ii}^{1}-E)c_{i1}+\sum_{j\neq i}(\gamma_{ij}^{1*}c_{j2}+\alpha_{ij}^{1}c_{j1})=0, \tag{6.2c}$$

where

$$\langle\Phi_{in}'|H|\Phi_{j,n-1}\rangle=\beta_{ij}\delta(\mathbf{k}_{\parallel}-\mathbf{k}_{\parallel}') \quad (n>2), \tag{6.3a}$$

$$\langle\Phi_{in}'|H|\Phi_{j,n+1}\rangle=\gamma_{ij}^{*}\delta(\mathbf{k}_{\parallel}-\mathbf{k}_{\parallel}') \quad (n>1), \tag{6.3b}$$

$$\langle\Phi_{in}'|H|\Phi_{jn}\rangle=\alpha_{ij}\delta(\mathbf{k}_{\parallel}-\mathbf{k}_{\parallel}') \quad (n>1), \tag{6.3c}$$

$$\langle\Phi_{i2}'|H|\Phi_{j1}\rangle=\beta_{ij}^{1}\delta(\mathbf{k}_{\parallel}-\mathbf{k}_{\parallel}'),$$

$$\langle\Phi_{i1}'|H|\Phi_{j1}\rangle=\alpha_{ij}^{1}\delta(\mathbf{k}_{\parallel}-\mathbf{k}_{\parallel}'), \tag{6.3d}$$

$$\langle\Phi_{i1}'|H|\Phi_{j2}\rangle=\gamma_{ij}^{1*}\delta(\mathbf{k}_{\parallel}-\mathbf{k}_{\parallel}'). \tag{6.3e}$$

We note[27] from Eq. (6.3) that $\gamma_{ij}=\beta_{ji}$ and $\gamma_{ij}^{1}=\beta_{ji}^{1}$. Matrix elements such as β_{ij} are sometimes complex valued.[25]

We introduce Mz transforms $F_i(z)$

$$F_i(z)=\sum_{1}^{\infty}c_{in}z^{1-n}, \quad (i=1 \text{ to } M) \tag{6.4}$$

and inversion formulas

$$c_{in}=\frac{1}{2\pi i}\oint F_i z^{n-2}\,dz, \quad (i=1 \text{ to } M) \tag{6.5}$$

apply them to Eqs. (6.1)–(6.2). The result, in matrix notation, is

$$[\mathbf{z}^2\mathbf{G}^{*}+z(\mathbf{A}-E\mathbf{I})+\mathbf{B}]\mathbf{F}=[z^2\mathbf{G}^{*}+z(\mathbf{A}-E\mathbf{I})+\mathbf{B}-\mathbf{B}_1]\mathbf{c}_1+z\mathbf{G}^{*}\mathbf{c}_2 \tag{6.6}$$

and for the boundary condition (6.2c)

$$\mathbf{G}_1^{*}\mathbf{c}_2+(\mathbf{A}_1-E\mathbf{I})\mathbf{c}_1=0, \tag{6.7}$$

where $\mathbf{F}$, $\mathbf{c}_1$, and $\mathbf{c}_2$ denote column vectors whose components are F_i, c_{i1}, and c_{i2} ($i=1$ to M), respectively. $\mathbf{A}$, $\mathbf{A}_1$, $\mathbf{B}$, and $\mathbf{B}_1$ denote $\mathbf{M}\times\mathbf{M}$ matrices, with elements α_{ij}, α_{ij}^{1}, β_{ij}, and β_{ij}^{1}, while the elements of $\mathbf{G}^{*}$ and $\mathbf{G}_1^{*}$ are given by

$$(\mathbf{G}^{*})_{ii}=\beta_{ii}^{*}, \quad (\mathbf{G}^{*})_{ij}=\gamma_{ij}^{*}=\beta_{ji}^{*} \quad (j\neq i), \tag{6.8a}$$

$$(\mathbf{G}_1^{*})_{ii}=\beta_{ii}^{1*}, \quad (\mathbf{G}_1^{*})_{ij}=\gamma_{ij}^{1*}=\beta_{ji}^{1*} \quad (j\neq i). \tag{6.8b}$$

Equations (6.6)–(6.7) yield

$$\mathbf{F}=\mathbf{I}c_1-[\mathbf{z}^2\mathbf{G}^{*}+z(\mathbf{A}-E\mathbf{I})+\mathbf{B}]^{-1}\times[\mathbf{B}_1+z\mathbf{G}^{*}\mathbf{G}_1^{*-1}(\mathbf{A}_1-E\mathbf{I})]\mathbf{c}_1, \tag{6.9}$$

where $\mathbf{I}$ is the unit matrix. Equations (6.5), (6.6), and (6.9) represent the extension of Eqs. (3.1), (3.2), and (4.2) to the coupled multi-band case.

In applying Eq. (6.9) it is necessary to find the poles on the unit circle. They occur at

$$\det|\mathbf{z}^2\mathbf{G}^{*}+z(\alpha-E\mathbf{I})+\mathbf{B}|=0 \tag{6.10}$$

which is a polynomial in z of degree $2M$.

The poles on the unit circle can be found by introducing the transformation[28]

$$w=i(z-1)/(z+1) \tag{6.11}$$

which transforms the unit circle, $z=\exp(i\theta)$ into the real axis, since w equals $\tan(\theta/2)$, and the interval $(-\pi<\theta<\pi)$ corresponds to $(-\infty<w<\infty)$. Since standard programs are available for locating the poles on the real axis, one can find the roots in Eq. (6.10) on the unit circle. With the transformation (6.11), Eq. (6.10) becomes a polynomial in w of degree $2M$. In this way, a solution for the multiband TB approximation with complex coefficients has been obtained.

VII. COUNTING OF STATES

One reason for using a box type normalization, I am told, is to assist in the counting of the electronic states in treating various phenomena. We consider this counting using the present continuous normalization, for applications of current interest. The systems so treated involve interfacial electron transfer with weak electronic interaction between a metal M_1 and the second reactant M_2, weak typically because of an adsorbed insulating layer on M_1. The subsystem M_1 plus the adsorbate will be treated as a single entity.

The forward rate of electron transfer in the weak interaction case, from a particular occupied electronic state n of M_1 to a particular unoccupied electronic state of M_2, is proportional to the square of an electronic matrix element

of some operator H. If $\Phi_n^{(1)}$ and $\Phi_m^{(2)}$ denote electronic states of M_1 and M_2, respectively, and if $f(E_n^{(1)})$ denotes the Fermi Dirac distribution function, then the rate of electron transfer from M_1 as a whole to a particular unoccupied state m of M_2, $R(M_1 \rightarrow m^{(2)})$, has the proportionality

$$R(M_1 \rightarrow m^{(2)}) \propto \sum_n |\langle \Phi_m^{(2)}|H|\Phi_n^{(1)}\rangle|^2 f(E_n^{(1)}) \quad (7.1)$$

when a box type normalization $\langle \Phi_n^{(1)}|\Phi_{n'}^{(1)}\rangle = \delta_{nn'}$ is used. If, instead, the normalization in Eq. (2.15) is used, this sum over n is replaced by an integral over $\mathbf{k}^{(1)}$

$$R(M_1 \rightarrow m^{(2)}) \propto \int \mathbf{dk}^{(1)} |\langle \Phi_m^{(2)}|H|\Phi_{\mathbf{k}}^{(1)}\rangle|^2 f(E_{\mathbf{k}}^{(1)}). \quad (7.2)$$

If M_2 is also a metal or semiconductor, the net forward ET rate from M_1 to M_2, $R(M_1 \rightarrow M_2)$ is obtained by multiplying Eq. (7.2) by the probability that the state $m^{(2)}$ is unoccupied, $1-f(E_m^{(2)})$, and summing over $m^{(2)}$. Or if, instead, the normalization in Eq. (2.15) is used, this sum is replaced by an integral over $k^{(2)}$

$$R(M_1 \rightarrow M_2) \propto \int\int \mathbf{dk}^{(1)}\, \mathbf{dk}^{(2)} |\langle \Phi_{\mathbf{k}}^{(2)}|H|\Phi_{\mathbf{k}}^{(1)}\rangle|^2 f \times (E_{\mathbf{k}}^{(1)})[1-f(E_{\mathbf{k}}^{(2)})]. \quad (7.3)$$

Analogous remarks apply to the reverse process. The Fermi energy of the bulk solid itself is found, after solving for the band structure $E(\mathbf{k})$, by sampling k points in the Brillouin zone, ordering them with respect to energy, and successively filling them until the fraction occupied equals (the number of electrons per unit cell)/(twice the number of atomic orbitals per unit cell).

Applications of these expressions are made elsewhere. In these applications, it is necessary to have some estimate of the energy difference between the Fermi level of the metal and an orbital energy of the adsorbate itself, for example, the lowest unoccupied or highest occupied electronic state of the adsorbed layer. Even much more accurate calculations cannot be expected to capture this difference adequately for layers involving large adsorbate molecules. As one way for obtaining it we first recall that in the case of electron or hole transfer in molecules or proteins it was sometimes possible to find the energy of a donor or acceptor orbital relative to that of a bridge orbital by using the charge transfer spectrum[29] of the donor/bridge subsystem or acceptor/bridge subsystem. In the present case, obtaining such solid/adsorbate charge transfer spectra will be more difficult, but could perhaps be explored using thin films, or other interfacial methods. Alternatively, work functions and ionization potentials could be utilized as an expedient. Finally, we note that in typical applications, it will be assumed that the edge-to-edge distance between the adsorbed layer and the second reactant (an ion close to or chemically attached to the adsorbed layer or in STM, a nearby metal tip) is small enough that the long-range asymptotic form of the wave function may play no major role.

VIII. CONCLUDING REMARKS

A method of obtaining orbital solutions in the tight-binding approximation for semi-infinite solids is described. A transform method and delta function normalization are used. The results are applied elsewhere to various electron transfer problems at interfaces. A comparison with other semi-infinite methods which could be adapted to these problems will be of interest.

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APPENDIX: DELTA FUNCTION REPRESENTATION AND CONSEQUENCES

The result (2.11)[24] can be obtained using the exponential Fourier series for a periodic function $f(\theta)$ with period 2π

$$f(\theta) = \sum_{-\infty}^{\infty} e^{in\theta} f_n, \quad f_n = \frac{1}{2\pi}\int_{-\pi}^{\pi} e^{-in\theta} f(\theta)\, d\theta, \quad (A1)$$

where the f_n are the Fourier coefficients. When $f(\theta)$ is chosen to be the infinite periodic sum

$$f(\theta) = \sum_{m=-\infty}^{\infty} \delta(\theta - 2\pi m). \quad (A2)$$

f_n in the second equality in Eq. (A1) becomes $1/2\pi$. The first equality then yields Eq. (2.11).

From Eq. (2.11) are obtained the following expressions, used in the normalization (4.8) of the c_n coefficients (4.7).

$$\sum_{n=2}^{\infty} \sin(n-m)\theta \sin(n-m)\theta' = \frac{\pi}{2}[\delta(\theta-\theta') - \delta(\theta+\theta')] - \delta_{m0} \sin\theta \sin\theta' \quad (m=0,1,2), \quad (A3)$$

$$\sum_{n=2}^{\infty} [\sin n\theta \sin(n-m)\theta' + \sin n\theta' \sin(n-m)\theta] = \pi \cos m\theta [\delta(\theta-\theta') - \delta(\theta+\theta')] + \delta_{m2} \sin\theta \sin\theta' \quad (m=1,2), \quad (A4)$$

$$\sum_{n=2}^{\infty} [\sin(n-1)\theta \sin(n-2)\theta' + \sin(n-1)\theta' \sin(n-2)\theta] = \pi \cos\theta [\delta(\theta-\theta') - \delta(\theta+\theta')]. \quad (A5)$$

In each case, the $\delta(\theta+\theta')$ is then omitted, because θ and θ' are both confined to the $(0,\pi)$ interval.

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[23] This k corresponds to the usual ratio of integers which appears in box type normalizations, m/N. Here N is the number of sites in the box, and so equals the number of wave functions in a band, and m is an integer labeling each wave function.

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[26] This transformation then involves seeking the poles in a small circle about $w=0$. When $n=1$, it may be verified from Eq. (4.3) by expansion in powers of w that no such pole exists and hence that the integral vanishes. For $n>1$, poles do exist, and so the integral is then nonzero.

[27] Interchanging the prime and unprimed symbols in the left side of Eq. (6.3a) produces a similar effect on the right side. The statements then follow from the definitions of β_{ij} and γ_{ij} in Eqs. (6.3a)–(6.3b) and from Eqs. (6.3d)–(6.3e).

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