



Tight-binding methods for the study of surface states on semiconductors
by William Arthur Schwalm

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF
PHILOSOPHY in PHYSICS

Montana State University

© Copyright by William Arthur Schwalm (1978)

Abstract:

The unifying concept which relates essentially all of the methods which currently appear in the literature for computing surface electronic structure from a given, tight-binding Hamiltonian is shown to be the difference equations satisfied by the Green functions. An efficient, generating function formalism is developed through which the analytic resolvent method of Levine and Freeman may be extended in order to solve more realistic surface problems. Two model Hamiltonians are completely solved in order to demonstrate this method: One in which there is one state per layer and an s-p Hamiltonian with one s-like and one p-like state per layer.

With the aid of the solution of the s-p Hamiltonian, a simple, bulk, bond-orbital model is introduced and it is seen that there is a limit in which this approximation is exact. This model is used to assess a bulk, bond-orbital model approach to the surface problem.

A bulk, bond-orbital model proposed by Pantelides and Harrison is used to study eigenstates of a twelve layer film of (110) GaAs. The results compare well with those of calculations which do not make bond-orbital approximations. Results are discussed and compared with those of other investigations.

TIGHT-BINDING METHODS FOR THE STUDY
OF SURFACE STATES ON SEMICONDUCTORS

by

WILLIAM ARTHUR SCHWALM

A thesis submitted in partial fulfillment
of the requirements for the degree

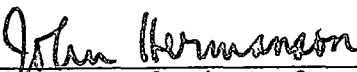
of


DOCTOR OF PHILOSOPHY


in

PHYSICS

Approved:


Chairman, Graduate Committee


Head, Major Department


Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

June, 1978

ACKNOWLEDGMENTS

The author gladly takes this opportunity to thank Dr. John Hermanson who suggested and coordinated the research reported here as part of the effort of our group in theoretical surface studies. He also wishes to thank Dr. Hermanson for unlimited time spent in discussing a large number of topics in modern physics. His advice and patient and skillful direction have always been deeply appreciated.

Sincere thanks also to Mizuho Kawajiri for many interesting discussions and a great deal of help with practical matters, and to Dr. Gerald Lapeyre for continuing encouragement and support.

Thanks to the members of the photoemission spectroscopy group for many enlightening and stimulating discussions, and special thanks to Dr. James Anderson for a careful reading and constructive criticism of this thesis.

TABLE OF CONTENTS

| | Page |
|--|------|
| VITA | ii |
| ACKNOWLEDGMENTS | iii |
| LIST OF FIGURES | vi |
| ABSTRACT | viii |
| I. INTRODUCTION | 1 |
| A. Matrix Slab Calculations | 1 |
| B. Green Function Calculations | 3 |
| II. ONE-BAND CASE | 6 |
| A. Bulk Hamiltonian | 6 |
| B. Layer Orbitals | 7 |
| C. Green Functions | 8 |
| 1. Bulk | 8 |
| 2. Surface | 11 |
| D. Relation Between Green Functions and Densities and Densities of States | 11 |
| E. Relation Between J and G | 13 |
| F. Methods of Solution | 15 |
| 1. Transfer Matrix Method | 15 |
| 2. Effective Potential Method | 17 |
| 3. Analytic Resolvent Method | 19 |
| III. TWO-BAND CASE | 33 |
| A. s-p Band, Normal Emission | 33 |
| 1. Bulk | 33 |

| | Page |
|--|------|
| 2. Surface | 52 |
| B. Simple Bond-Orbital Model | 53 |
| 1. Bulk | 53 |
| 2. Surface | 62 |
| IV. BOND-ORBITAL MODEL OF HARRISON | 69 |
| A. Bulk Chemistry | 69 |
| 1. Formation of bond-orbitals | 69 |
| 2. Bond-orbital matrix elements | 75 |
| B. Surface Definition | 78 |
| 1. Surface matrix elements | 78 |
| 2. Bravais lattice | 80 |
| 3. Layer-orbitals | 83 |
| V. MATRIX SLAB CALCULATION | 85 |
| A. Implementation | 85 |
| 1. Bulk | 85 |
| 2. Surface | 85 |
| B. Results and Discussion | 86 |
| VI. SUMMARY AND CONCLUSION | 101 |
| A. Generating Function Formalism | 101 |
| B. Thin Film Calculation | 109 |
| REFERENCES | 113 |
| APPENDIX A - Bulk Matrix Elements | 117 |
| APPENDIX B - Layer Orbital Matrix Elements | 120 |
| APPENDIX C - Coupling of Surface to Bulk | 123 |

LIST OF FIGURES

| Figure | Page |
|---|------|
| 1. Argand Diagram for One-Band Model | 24 |
| 2. Layer Densities of States for the One-Band Model | 28 |
| 3. Incoherent Sums for the One-Band Model | 32 |
| 4. Bands for the s-p Model | 40 |
| 5. Roots of the Two-Band Characteristic Polynomial | 45 |
| 6. Two-Band Bulk Density of States | 51 |
| 7. Layer Densities for the s-p Model | 54 |
| 8. Formation of a Chemical Bond | 56 |
| 9. Bond-Orbital Approximation for Gap State Energy | 65 |
| 10. Hybrid Orbitals in a Zincblende Semiconductor | 69 |
| 11. Tetrahedron of Bond-Orbitals | 76 |
| 12. Formation of Zincblende Structure | 77 |
| 13. Bond-Orbital Matrix Elements | 79 |
| 14. Bulk-to-Surface Coupling Coefficients | 81 |
| 15. Basis for the fcc Lattice | 82 |
| 16. Result of Truncating the Bulk | 87 |
| 17. More Realistic Surface | 88 |
| 18. Surface Brillouin Zone | 89 |
| 19. Filled Surface States on GaAs (110) | 91 |
| 20. Probability Distribution for B_1 | 92 |

| Figure | Page |
|---|------|
| 21. Probability Distribution for B_2 | 94 |
| 22. Probability Distribution for B_3 | 96 |
| 23. Bulk Layer Density of States for GaAs (110) | 105 |
| 24. s-like Part of the Layer Densities for the s-p Model | 107 |

ABSTRACT

The unifying concept which relates essentially all of the methods which currently appear in the literature for computing surface electronic structure from a given, tight-binding Hamiltonian is shown to be the difference equations satisfied by the Green functions. An efficient, generating function formalism is developed through which the analytic resolvent method of Levine and Freeman may be extended in order to solve more realistic surface problems. Two model Hamiltonians are completely solved in order to demonstrate this method: One in which there is one state per layer and an s-p Hamiltonian with one s-like and one p-like state per layer.

With the aid of the solution of the s-p Hamiltonian, a simple, bulk, bond-orbital model is introduced and it is seen that there is a limit in which this approximation is exact. This model is used to assess a bulk, bond-orbital model approach to the surface problem.

A bulk, bond-orbital model proposed by Pantelides and Harrison is used to study eigenstates of a twelve layer film of (110) GaAs. The results compare well with those of calculations which do not make bond-orbital approximations. Results are discussed and compared with those of other investigations.

I. INTRODUCTION

Recently, many calculations of surface densities of states have been performed within the tight-binding interpolation scheme¹⁻¹⁴. According to this method, the single-electron Hamiltonian operator is represented by a set of matrix elements between localized states centered at each atomic site. Ultimately, these matrix elements are treated as parameters and are selected in such a way as to reproduce certain results of more ambitious calculations or of experimental measurements¹⁵. For example, the parameters are often chosen to reproduce the bulk band structure.

From the bulk Hamiltonian matrix elements, the program for computing the change in the density of states caused by the presence of the surface usually proceeds along one of two ways: Either a matrix Hamiltonian corresponding to a large slab of material is diagonalized, or Green functions are computed for the semi-infinite crystal.

A. Matrix Slab Calculations

The first path along which the calculation might proceed involves the diagonalization of a large matrix¹⁻³. This corresponds to solving exactly the problem of finding the quantum states of a thin slab consisting of several atomic layers. Translation symmetry in the directions parallel to the surface is preserved, and thus the matrix diagonalization problem reduces to finite blocks corresponding to the

irreducible representations of the surface translation group; in other words, the surface perturbation does not mix those eigenstates of the bulk which have different components $k_{||}$ of wave vector parallel to the surface.

The great advantage of a slab type of calculation is that it is easily implemented. For a given value of $k_{||}$, the matrix is filled and numerically diagonalized. The energy eigenvalues and corresponding eigenvectors may thus be obtained.

There are three major objections to the large matrix method. First, for a particular choice of $k_{||}$, the large matrix would be of rank nN , where n is the number of localized orbitals per unit cell, and N is the number of layers. If there is a reflection symmetry through the center of the slab, the rank may be reduced to $nN/2$.

There will be only nN energy eigenvalues for each choice of $k_{||}$; thus it is difficult to produce enough eigenvalues to construct a layer-by-layer density of states for a particular value of $k_{||}$, as one would wish to do in order to compare with the results of an angle-resolved photoemission spectroscopy experiment.

As an example of this difficulty, consider a rather large slab of 15 layers ($N=15$) and eight states on each layer ($n=8$). Then the matrix will be 120×120 and there will be 120 energy eigenvalues in all. This will create a rather sketchy histogram when these energy values are partitioned into, say, 10 boxes over the entire energy range of

the spectrum.

The second objection is that the rank of the matrix is large enough so that the diagonalization must be done numerically. The solutions do not provide any analytical insight into the nature of the surface states.

One final objection is that even as the slab gets larger, the surface features of the spectrum become lost in the bulk part which grows with N . Extra steps would be required in order to project the density of states onto the surface layer.

B. Green Function Calculations

The second line along which tight-binding calculations have evolved is the resolvent or Green function method⁵⁻⁸. Here again the problem is reduced by the translation symmetry along the surface. This time, however, the semi-infinite crystal is treated.

For the tight-binding Hamiltonians, the equations of motion for the Green functions become a set of coupled, linear difference equations with constant coefficients. These equations may be solved in one of a number of ways, and a layer-by-layer density of states can be calculated from the imaginary parts of the various Green functions. The different methods of solving the difference equations have been given different names such as the analytic resolvent method¹⁶, the transfer matrix method¹⁷, the ansatz method¹⁸ or the effective

potential method¹⁹. Each method gives rise to another vocabulary, but the unifying concept is the set of difference equations for the Green functions.

The first criticism of the matrix method is automatically avoided when the resolvent method is used. The Green function method easily produces the continuum as well as the discrete part of the spectrum, since the semi-infinite crystal is treated.

The use of Green functions may also avoid the second criticism of the matrix method, provided that closed form solutions of the equations of motion can be found. The difference equations possess solutions in closed form only if the tight-binding Hamiltonian is simple enough. The existence of solutions in terms of elementary functions cannot depend upon the method of solution. With each model Hamiltonian is associated a characteristic polynomial, the degree of which is determined by the complexity of the model. When this characteristic polynomial falls outside the class of polynomials which are solvable by radicals, then a solution in terms of elementary functions does not exist. The polynomial is the characteristic polynomial of the system of difference equations which are the equations of motion.

Even when a solution in closed form in terms of elementary functions does not exist, the Green function method may lead to some analytical insight in the following way. The layer densities of states follow from Green functions which are expressible as rational functions

of the roots of the characteristic polynomials. Near a singularity, they may be expanded and their behavior related to the motion of the roots in the complex plane, thereby providing a connection between the bulk and surface electronic structures.

To be fair, it must be admitted that even in the cases when exact solutions are possible, there is sometimes little motivation to write them down because their formal complexity may render them incomprehensible⁵⁻⁶. None-the-less, these solutions, whether symbolic or partly numerical, represent in a most convenient form essentially exact solutions to the given model Hamiltonian for the semi-infinite geometry.

Part of the convenience of the Green functions is that the density of states is naturally obtained in a form which is factored according not only to the individual layers, but also according to the individual orbitals on each layer. The final objection to the matrix method is thus circumvented by the Green function method.

II. ONE-BAND CASE

A. Bulk Hamiltonian

The purpose of this section is to introduce one of the simplest problems which may be solved by the resolvent method and thus to demonstrate the unity of various solution procedures for the resulting difference equations.

Consider a crystal with simple cubic structure consisting of an s-like atomic orbital at each site. The basis functions are represented by $|\ell, m, n\rangle$, where the position of the site is $\vec{r} = a\ell\hat{x} + am\hat{y} + an\hat{z}$. The lattice spacing is a and $\hat{x}, \hat{y}, \hat{z}$ are Cartesian unit vectors. The indices ℓ, m, n are integers and specify the position of the site.

In this basis, then, the bulk Hamiltonian is defined as follows:

$$\begin{aligned}
 \langle \ell' m' n' | H^{(0)} | \ell m n \rangle &= U \delta_{\ell\ell'} \delta_{mn'} \delta_{nn'} \\
 &+ \mu \delta_{\ell'\ell} \delta_{m'm} (\delta_{n'n+1} + \delta_{n'n-1}) \\
 &+ \mu \delta_{\ell'\ell} (\delta_{m'm+1} + \delta_{m'm-1}) \delta_{n'n} \\
 &+ \mu (\delta_{\ell'\ell+1} + \delta_{\ell'\ell-1}) \delta_{m'm} \delta_{n'n},
 \end{aligned} \tag{1}$$

where U and μ are integrals

$$\begin{aligned}
 U &= \int \phi_S^*(\vec{x}) H^{(0)}(\vec{x}) \phi_S(\vec{x}) d^3x, \\
 \mu &= \int \phi_S^*(\vec{x}) H^{(0)}(\vec{x}) \phi_S(\vec{x}-a\hat{x}) d^3x.
 \end{aligned} \tag{2}$$

In fact, we treat the integrals U and μ as constants which are

adjusted to produce the bulk band structure which may be computed by another means. It is assumed that all other matrix elements of the Hamiltonian vanish and also that

$$\langle \ell' m' n' | \ell m n \rangle = \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n}. \quad (3)$$

B. Layer Orbitals

If an angle-resolved photoemission experiment were to be performed on a (100) surface of the hypothetical crystal defined above, then the angle-resolved density of initial states might be of interest.

Advantage may be taken of the translation symmetry in the plane of the surface if the bulk Hamiltonian is rewritten in terms of a new basis which has Bloch symmetry along the \hat{y} and \hat{z} directions.

Suppose for the moment that each layer is finite and consists of N atoms in the \hat{y} direction and N atoms in the \hat{z} direction. Ultimately, one could take the limit $N \rightarrow \infty$, but this will not be necessary, since N will cancel out of the equations.

Define a layer orbital on layer ℓ by the relation

$$|\ell, k_y, k_z\rangle = \frac{1}{N} \sum_{mn} e^{ik_y am} e^{ik_z an} |\ell, m, n\rangle. \quad (4)$$

The transformation is unitary and thus the layer orbitals are orthonormal.

$$\langle \ell', k'_y, k'_z | \ell, k_y, k_z \rangle = \delta_{\ell' \ell} \delta_{k'_y k_y} \delta_{k'_z k_z}. \quad (5)$$

Because of translation symmetry, H does not mix layer orbitals

of different wave vector, since these orbitals would then belong to different irreducible representations of the two-dimensional translation group. Thus, H is diagonal with respect to k_y, k_z . From the definition (4) of the layer orbitals and from expression (1) for the bulk Hamiltonian matrix elements,

$$\langle \ell', k'_y, k'_z | H^{(0)} | \ell, k_y, k_z \rangle = \delta_{k'_y, k_y} \delta_{k'_z, k_z} [\epsilon(k_y, k_z) \delta_{\ell', \ell} + \mu(\delta_{\ell', \ell+1} + \delta_{\ell', \ell-1})] \quad (6)$$

where $\epsilon(k_y, k_z) = U + 2\mu \cos k_y a + 2\mu \cos k_z a$. For a particular k_y, k_z , we have a one-dimensional problem associated with the Hamiltonian

$$H_{\ell', \ell}^{(0)} = \epsilon \delta_{\ell', \ell} + \mu(\delta_{\ell', \ell+1} + \delta_{\ell', \ell-1}). \quad (7)$$

This bulk Hamiltonian is connected to the surface Hamiltonian in a rather simple way. Suppose, without loss of generality, that the surface layer is $\ell = 1$. Then the Hamiltonian becomes

$$H_{\ell', \ell} = \epsilon \delta_{\ell', \ell} + \mu(\delta_{\ell', \ell+1} + \delta_{\ell', \ell-1})$$

when

$$\ell', \ell > 1; H_{11} = \epsilon, H_{12} = H_{21} = \mu. \quad (8)$$

$$H_{\ell', \ell} = 0 \text{ otherwise.}$$

C. Green Functions

1. Bulk. The common methods of solution involve the use of one of two types of Green functions.

The first type is a Green function for the bulk Hamiltonian. Let b_{ℓ}^+ , b_{ℓ} create and destroy an electron in layer orbital ℓ for a given value of k_y, k_z . The time dependence of b_{ℓ} and b_{ℓ}^+ in the Heisenberg picture is governed by the bulk Hamiltonian $H^{(0)}$. Then the one-electron bulk Green function between layer ℓ and layer ℓ' is defined by²⁰

$$G_{\ell',-\ell}(t) = \langle\langle b_{\ell'}; b_{\ell} \rangle\rangle = -i\theta(t) \langle 0 | \{b_{\ell'}(t), b_{\ell}^+(t=0)\} | 0 \rangle. \quad (9)$$

In equation (9), $|0\rangle$ is the state with no electrons in the crystal, $\theta(t)$ is a step function equal to 0 if $t < 0$, $\frac{1}{2}$ if $t=0$, and 1 if $t > 0$. The bracket is an anticommutator with the usual definition:

$$\{A, B\} = AB + BA \quad (10)$$

It should be noted here that the bulk Green functions $G_{\ell',-\ell}(t)$ are only functions of the layer difference $\ell'-\ell$, rather than of ℓ' or ℓ separately, because of translation symmetry.

The operator $b_{\ell}(t)$ evolves according to the Heisenberg equation

$$i \frac{d}{dt} b_{\ell}(t) = [b_{\ell}(t), H^{(0)}]. \quad (11)$$

Thus, $G_{\ell',-\ell}(t)$ satisfies

$$i \frac{d}{dt} G_{\ell',-\ell}(t) = \delta(t) \langle 0 | \{b_{\ell'}(0), b_{\ell}^+(0)\} | 0 \rangle - \langle\langle [H^{(0)}, b_{\ell'}]; b_{\ell} \rangle\rangle, \quad (12)$$

where the first term on the right is just $\delta(t)\delta_{\ell',\ell}$ because

$$\{b_{\ell'}, b_{\ell}^+\} = \delta_{\ell',\ell}. \quad (13)$$

The second term on the right of equation (11) is a higher order Green function

$$\begin{aligned} <<[H^{(0)}, b_{\ell'}]; b_{\ell}^+ >> = \\ -i\theta(t) <0| \{ [H^{(0)}, b_{\ell'}(t)], b^+(t=0) \} |0>. \end{aligned} \quad (14)$$

Introducing the Fourier transform

$$G_{\ell' - \ell}(\omega) = \int_{-\infty}^{\infty} G_{\ell' - \ell}(t) e^{-i\omega t} dt, \quad (15)$$

and noting that in this case the higher order Green function is a linear combination of the original one electron Green functions, equation (12) becomes

$$\begin{aligned} \omega G_{\ell' - \ell}(\omega) &= \delta_{\ell' \ell} + \mu G_{\ell' + \ell - 1}(\omega) \\ + \epsilon G_{\ell' - \ell}(\omega) &+ \mu G_{\ell' - 1 - \ell}(\omega). \end{aligned} \quad (16)$$

This difference equation is the equation of motion of the bulk Green functions.

It is important to notice that for one-electron Hamiltonians like this one, the Green functions in the domain are matrix elements of the resolvent operator defined by

$$G = (\omega - H^{(0)})^{-1} \quad (17)$$

At points in the ω -plane where G is not well-defined (the spectrum of $H^{(0)}$) it can be seen from (14) and (15) that G should be considered as the limit as $\eta \rightarrow 0^+$ of $(\omega + i\eta - H^{(0)})^{-1}$. Using (17),

$$\sum_{\ell''} (\omega + i\eta - H^{(0)})_{\ell'\ell''} G_{\ell''-\ell} = \delta_{\ell'\ell}. \quad (18)$$

This is exactly equivalent to equation (16).

2. Surface. Another type of Green function which is used contains the effect of the surface and is defined as

$$J_{\ell'\ell}(t) = -i\theta(t) \langle 0 | \{a_{\ell'}(t), a_{\ell}^+(0)\} | 0 \rangle. \quad (19)$$

The time evolution of a_{ℓ}^+ and a_{ℓ} is due to the full Hamiltonian H which is truncated at the surface. Thus

$$J_{\ell'\ell}(\omega) = \langle \ell' | (\omega - H)^{-1} | \ell \rangle. \quad (20)$$

H is equivalent to $H^{(0)}$ but truncated at the surface according to (8).

$J_{\ell'\ell}$ is not a function only of $\ell'-\ell$, because of the lack of translation symmetry.

D. Relation Between Green Functions and Densities of States

The density of states function for a system governed by a Hamiltonian H is defined as

$$D(E) = \sum_{\nu} \delta(E - E_{\nu}). \quad (21)$$

The index ν runs over each individual eigenstate of H . $D(E)$ is so defined as to enable a sum over ν to be converted to an integral over E .

$$\sum_{\nu} f(E_{\nu}) = \int f(E) D(E) dE. \quad (22)$$

The delta functions in (21) may be represented by

$$\begin{aligned} \delta(E-E_{\nu}) &= \lim_{\eta \rightarrow 0^+} \frac{1}{\pi} \frac{\eta}{(E-E_{\nu})^2 + \eta^2} \\ &= \lim_{\eta \rightarrow 0^+} \frac{1}{\pi} \{- \text{Im.} \left(\frac{1}{E + i\eta - E_{\nu}} \right)\}. \end{aligned} \quad (23)$$

From this point on, the $\lim_{\eta \rightarrow 0^+}$ will not be written explicitly.

$$\begin{aligned} D(E) &= - \frac{1}{\pi} \text{Im.} \sum_{\nu} \frac{1}{E + i\eta - E_{\nu}} \\ &= - \frac{1}{\pi} \text{Im.} \left(\sum_{\nu} \langle \nu | \frac{1}{E + i\eta - H} | \nu \rangle \right) \\ &= - \frac{1}{\pi} \text{Im.} (\text{Trace } J). \end{aligned} \quad (24)$$

Rather than the total density of states $D(E)$, it is often more convenient to have the projected density of states for some state $|j\rangle$, where $|j\rangle$ is quite arbitrary and not an eigenstate of H .

$$D_j(E) = \sum_{\nu} |\langle \nu | j \rangle|^2 \delta(E-E_{\nu}). \quad (25)$$

This would permit evaluation of projected sums of the form

$$\sum_{\nu} |\langle j | \nu \rangle|^2 f(E_{\nu}) = \int D_j(E) f(E) dE. \quad (26)$$

As an example, the local density of states

$$D_{\ell}(E) = \sum_{\nu} |\langle \ell | \nu \rangle|^2 \delta(E-E_{\nu}) \quad (27)$$

is of interest in surface problems when ℓ is a layer orbital close to the surface for some value of k_y, k_z .

By the analysis above it follows that

$$D_{\ell}(E) = - \frac{1}{\pi} \text{Im.} J_{\ell\ell}(E) \quad (28)$$

For this reason, then, the object of the Green function method is to compute the diagonal part of the surface Green function J.

E. Relation Between J and G

The resolvent J corresponding to H must be related to the bulk resolvent G corresponding to $H^{(0)}$ via a perturbation V representing the effect of the surface. Evidently, V will not in any way be a small perturbation.

Let the layers of the crystal be separated into two classes: A will be the collection of all layers which will belong to the crystal after the surface is formed, and B will be the set of layer orbitals belonging to a barrier region. A scalar potential of magnitude $\frac{1}{p}$ will be added to each diagonal element of the Hamiltonian in the region B. In the limit that $p \rightarrow 0$, the solution will be excluded from region B and the boundary conditions in region A will have been changed from cyclic to standing-wave boundary conditions.

In the sample model studied here, B may be taken to consist of only one layer orbital, since this is sufficient to break all of the bonds at the surface. Take, for example, $\ell=0$, for B and let A consist of $\ell=1,2,3\dots$

Writing G and J in block form in the layer orbital basis,

$$G = \begin{pmatrix} G_{AA} & G_{AB} \\ G_{BA} & G_{BB} \end{pmatrix}, \quad V = \begin{pmatrix} 0 & 0 \\ 0 & \frac{1}{p} \end{pmatrix}. \quad (29)$$

$$J = (E-H^{(0)}-V)^{-1} = [(E-H^{(0)}) \cdot (1-GV)]^{-1} \quad (30)$$

$$J = (1-GV)^{-1}G, \text{ or } G = (1-GV) J. \quad (31)$$

Using (29), it follows

$$(1-GV) = \left(\begin{array}{c|cc} 1 & -\frac{1}{p} & G_{AB} \\ \hline 0 & 1-\frac{1}{p} & G_{BB} \end{array} \right) \quad (32)$$

Substituting (32) into (31) and using the block form

$$J = \left(\begin{array}{c|cc} J_{AA} & J_{AB} \\ \hline J_{BA} & J_{BB} \end{array} \right) \quad (33)$$

gives the two equations

$$J_{AA} - \frac{1}{p} G_{AB} J_{BA} = G_{AA}, \quad (34)$$

$$\left(1 - \frac{1}{p} G_{BB}\right) J_{BA} = G_{BA} \quad (35)$$

In the limit $p \rightarrow 0$, substitution of (35) into (34) yields²¹

$$J_{AA} = G_{AA} - G_{AB} (G_{BB}^{-1}) G_{BA} \quad (36)$$

Equation (36) is a very important relation which exists quite generally between the bulk and surface Green functions. It should be noted that equation (36) is an exact result and J_{AA} has now the effect of the new, standing-wave boundary conditions.

F. Methods of Solution

1. Transfer Matrix Method. This method was formulated by L. Falicov and F. Yndurain¹⁷ and has been extended by Mele and Joannopoulos¹⁴. The transfer matrix method is closely related to the ansatz¹⁸ method except that the latter name is usually applied to a method of directly solving the Hamiltonian eigenvalue problem

$$(E-H) |\psi\rangle = 0 \quad (37)$$

while the former name refers to the same method applied to the solution of the difference equations represented by the expression

$$(E-H) J = 1 \quad (38)$$

In both (37) and (38) the Hamiltonian includes the surface. (38) leads to a set of difference equations for the matrix elements of J. In the case of the simple model Hamiltonian of (8), these are

$$\sum_{\ell''} (E-H)_{\ell'\ell''} J_{\ell''\ell} = \delta_{\ell'\ell} \quad (39)$$

$$(E-\epsilon) J_{11} - \mu J_{21} = 1 \quad (40)$$

$$- \mu J_{11} + (E-\epsilon) J_{21} - \mu J_{31} = 0$$

$$- \mu J_{n1} + (E-\epsilon) J_{n+11} - \mu J_{n+21} = 0$$

$$(E-\epsilon) J_{12} - \mu J_{22} = 0 \quad (41)$$

$$- \mu J_{12} = (E-\epsilon) J_{22} = \mu J_{32} = 1$$

$$- \mu J_{n2} + (E-\epsilon) J_{n+12} = J_{n+22} = 0$$

etc.

The method of solution depends upon the fact that (40) is homogeneous for $n \geq 1$. Thus, for $n \geq 1$, the solution is a linear combination of powers of two numbers x_1, x_2 .

$$J_{n1} = A x_1^n + B x_2^n, \quad n \geq 1. \quad (42)$$

Try a solution $J_{n1} = x^n$. Then from (40) we have

$$\mu x^2 - (E - \epsilon)x + \mu = 0. \quad (43)$$

The function x here is what is known by Falicov and Yndurain¹⁷ as the transfer matrix, although in this simple example, it is not really a matrix.

This is the first example of a characteristic polynomial. The two roots are x_1 and x_2 .

$$x_{1,2} = \frac{E - \epsilon}{2\mu} \pm \left[\left(\frac{E - \epsilon}{2\mu} \right)^2 - 1 \right]^{1/2} \quad (44)$$

It can be seen from (43) that $x_1 x_2 = 1$. This is a general feature: roots of the characteristic equations occur in reciprocal pairs.

Suppose $E > \epsilon + 2$, then

$$|x_1| > 1 > |x_2|. \quad (45)$$

Since J_{n1} must be bounded as $n \rightarrow \infty$, the coefficient A of (42) must be zero. Whence:

$$J_{n1} = B x_2^n, \quad n \geq 1. \quad (46)$$

But, looking at the first of equations (40), we see that

$$(E-\epsilon) B x_2 - \mu B x_2^2 = 1, \quad (47)$$

$$B = \frac{1}{(E-\epsilon)x_2 - \mu x_2^2} = \frac{1}{\mu}. \quad (48)$$

At which expression (46) becomes

$$J_{n1} = \frac{x_2^n}{\mu}. \quad (49)$$

Now, the surface density of states follows from (49) via (28):

$$D_1(E) = \frac{1}{\pi\mu} \sqrt{1 - \left(\frac{E-\epsilon}{2\mu}\right)^2} \quad (50)$$

One could go back to equations (41) and solve for J_{22} and so on and thus find surface densities of states on each layer.

2. Effective Potential Method¹⁹. Another method for determining the layer density of states takes advantage of a kind of hidden symmetry of the total Hamiltonian H . This clever idea seems to be due to E-Ni Foo and et al.¹⁹. The connection of this method to the transfer matrix method was realized by Joannopoulos and Mele¹⁴.

Suppose we have solved the problem of finding the Green functions $J_{\ell'\ell}$ for the simple surface model above. Then, if we adsorb another layer orbital into position on $\ell=0$ which is exactly like the other layers and solve for the new Green functions $R_{\ell'\ell}$, we should find

$$R_{\ell'\ell} \equiv J_{\ell'+1, \ell+1}. \quad \text{By equation (31)}$$

$$(1 - JV) R = J,$$

$$\text{with } R = \left(\begin{array}{c|c} R_{00} & R_{01} \\ \hline R_{10} & R_{11} \end{array} \right), \quad (51)$$

$$J = \left(\begin{array}{c|c} \frac{1}{E-\epsilon} & 0 \\ \hline 0 & J_{11} \end{array} \right), \quad V = \left(\begin{array}{c|c} 0 & \mu \\ \hline \mu & 0 \end{array} \right) \quad (52)$$

Thus

$$(1-JV) = \left(\begin{array}{c|c} 1 & \frac{-\mu}{E-\epsilon} \\ \hline -\mu J_{11} & 1 \end{array} \right) \quad (53)$$

Whereupon (51) becomes

$$R_{00} - \frac{\mu}{E-\epsilon} R_{10} = \frac{1}{E-\epsilon}, \quad (54)$$

$$- \mu J_{11} R_{00} + R_{10} = 0. \quad (55)$$

Eliminating R_{10} between (54) and (55) and using $R_{00} = J_{11}$ gives

$$\frac{\mu^2}{E-\epsilon} J_{11}^2 + J_{11} - \frac{1}{E-\epsilon} = 0 \quad (56)$$

$$J_{11} = - \frac{E-\epsilon}{2\mu^2} \pm \frac{i}{\mu} \sqrt{1 - \left(\frac{E-\epsilon}{2\mu}\right)^2} \quad (57)$$

for $\epsilon - 2\mu < E < \epsilon + 2\mu$.

The minus sign in (57) must hold, in order that the density of states be positive, which means that

$$D_1(E) = \frac{1}{\pi\mu} \sqrt{1 - \left(\frac{E-\epsilon}{2\mu}\right)^2}. \quad (58)$$

Equation (58) agrees with (50).

An interesting note concerning the meaning of the effective potential method is the following:

The diagonal Green function $J_{\ell\ell}$ can be written in terms of an irreducible self energy $\Sigma_{\ell}(E)$:

$$J_{\ell\ell}(E) = (E - \epsilon - \Sigma_{\ell}(E))^{-1}. \quad (59)$$

(E) is the sum of all terms in the Neumann expansion²² in which ℓ does not occur in an intermediate state. For the simple case, the bulk Green function

$$G_{\ell-\ell}(E) = (E - \epsilon - \Sigma(E))^{-1} \quad (60)$$

contains a self energy $\Sigma(E)$ which is made up of a sum containing as intermediate states only layers to the right of a given layer ℓ and another sum over only layers to the left. Each sum is equal to $\frac{1}{2} \Sigma(E)$ because the bulk Hamiltonian connects only neighboring layers.

Thus

$$\Sigma_{\ell=1}(E) = \frac{1}{2} \Sigma(E) \quad (61)$$

holds at the surface layer.

3. Analytic Resolvent Method¹⁶. This application of scattering theory was made by S. Davison and J. D. Levine. The generating function formalism, which greatly facilitates computations as well as providing conceptual simplicity, is due to Schwalm, Hermanson and Kawajiri. Consider the bulk difference equation

$$-\mu G_{\ell+1} + (E-\epsilon) G_{\ell} - \mu G_{\ell-1} = \delta_{\ell 0}. \quad (62)$$

The analytic resolvent method consists of solving (62) in closed form and then applying (36). A more realistic model will lead to a more complicated system of bulk difference equations.

In order to introduce the generating function method, define a generating function:

$$f(x) = \sum_{\ell} x^{\ell} G_{\ell} \quad (63)$$

Multiplying (62) by x^{ℓ} and summing over ℓ while applying (63) yields

$$-\frac{\mu}{x} f + (E-\epsilon) f - x\mu f = 1 \quad (64)$$

or

$$f(x) = \frac{1}{(E-\epsilon) - \mu(x + \frac{1}{x})}. \quad (65)$$

The expression for G_{ℓ} will follow from (65) via a Laurent series expansion. But,

$$f(x) = -\frac{x}{\mu} \frac{1}{x^2 - \frac{E-\epsilon}{\mu} x + 1} \quad (66)$$

has three Laurent expansions. The roots of the denominator (which are zeros of the Fredholm determinant and roots of the characteristic polynomial of the difference equation)²⁹ are

$$x_{1,2} = \frac{E-\epsilon}{2\mu} \pm \sqrt{\left(\frac{E-\epsilon}{2\mu}\right)^2 - 1}. \quad (67)$$

These are the same roots appearing in (44). The generating function has become

$$\begin{aligned} f(x) &= -\frac{x}{\mu} \frac{1}{(x-x_1)(x-x_2)} \\ &= -\frac{x_1}{\mu} \frac{1}{(x_1-x_2)} \frac{1}{(x-x_1)} - \frac{x_2}{\mu} \frac{1}{(x_2-x_1)} \frac{1}{(x-x_2)}. \end{aligned} \quad (68)$$

The terms must be expanded in the following way:

$$(x-x_1)^{-1} = -\frac{1}{x_1} \left(1 + \frac{x}{x_1} + \frac{x^2}{x_1^2} + \dots\right) \text{ while} \quad (69)$$

$$(x-x_2)^{-1} = +\frac{1}{x} \left(1 + \frac{x_2}{x} + \frac{x_2^2}{x^2} + \dots\right). \quad (70)$$

These choices, which amount to a choice of the annulus of convergence of the Laurent expansion or equivalently to the choice of contour for the inversion integral

$$G_\ell = \frac{1}{2\pi i} \oint_C \frac{f(x)dx}{x^{\ell+1}} \quad (71)$$

follow from the physical boundary conditions on G_ℓ . Suppose by way of example that the alternative expansion had been made in x_1 rather than (69).

$$(x-x_1)^{-1} = \frac{1}{x} \left(1 + \frac{x_1}{x} + \frac{x_1^2}{x^2} + \dots\right). \quad (72)$$

Equation (72) indicates that $G_{-\ell} \sim x_1^\ell$ as $|\ell| \rightarrow \infty$. But from (45), $|x_1| > 1$. This is impossible for a physical solution, since G_ℓ must be bounded

in the bulk as $\ell \rightarrow \pm \infty$. Thus, the Laurent expansion is chosen to be convergent when $|x_2| < |x| < |x_1|$. The contour of integration in (71) may be chosen as $|x| = 1$. This choice of contour results from physical boundary conditions in the same way that the choice of the contour for inversion of the Fourier transform of a physical quantity is often specified by boundary conditions. Other choices for the Laurent expansion correspond to other solutions to the second order difference equation which are not in this case the right ones.

The above analysis has taken place under the supposition that $E > \epsilon + 2\mu$. The surd which appears in expressions (67) has branch points at $E = \epsilon \pm 2\mu$. Physically, these are van Hove singularities corresponding to the edges of the bulk energy band of this simple model. As E becomes lower than $\epsilon + 2\mu$, the radical must be continued past the branch point in such a way as to make it a smooth function of E . This is done by remembering the causality condition on $G_\ell(t)$ (see discussion following (17)) and replacing E by $E + i\eta$. In actual calculations for more realistic models, η is a small but finite, positive energy parameter. The choice of the branch cut is then taken so that

$$\sqrt{\left(\frac{E-\epsilon}{2\mu}\right)^2 - 1} = \frac{1}{2\mu} \sqrt{E - \epsilon - 2\mu} \sqrt{E - \epsilon + 2\mu}. \quad (73)$$

Notice that (73) is a branch cut convention and not an identity. The cuts for the two surd expressions on the right are along the real E axis toward $-\infty$, i.e., both phases are zero for large, positive real

energy. By this choice, a branch cut has been made using language a computer might understand, between the two bulk van Hove singularities which delimit a continuum. This general procedure has also been followed in later computations on realistic models where the continuum structure is far more complicated.

The trajectories of the roots x_1 and x_2 in the complex x -plane are presented in figure 1 with $\epsilon = 0$ and $\eta = .1\mu$. When η is quite small, the characteristic polynomial (43) has almost real coefficients. In that case, whenever x_1 and x_2 are complex, they are almost complex conjugates of one another. Therefore, because $x_2 = 1/x_1$, these roots would have the following form:

$$x_{1,2} = e^{\pm ika} e^{\pm \kappa a}, \quad (74)$$

where a is the crystal lattice spacing and ka and κa are real numbers with $0 < \kappa a \ll 1$. G_ℓ would have a damped, sinusoidal form as a function of ℓ .

$$G_\ell \propto e^{+i|\ell|ka} e^{-|\ell|\kappa a}. \quad (75)$$

The damping η goes to zero as $\eta \rightarrow 0^+$. Thus in the energy range $\epsilon - 2\mu < E < \epsilon + 2\mu$. G_ℓ corresponds to a discontinuous combination of two Bloch-like solutions to the homogeneous Hamiltonian eigenvalue problem:

$$(E-H) |\psi\rangle = 0. \quad (76)$$

It is the discontinuity in G_ℓ at $\ell=0$ which causes G to act as the

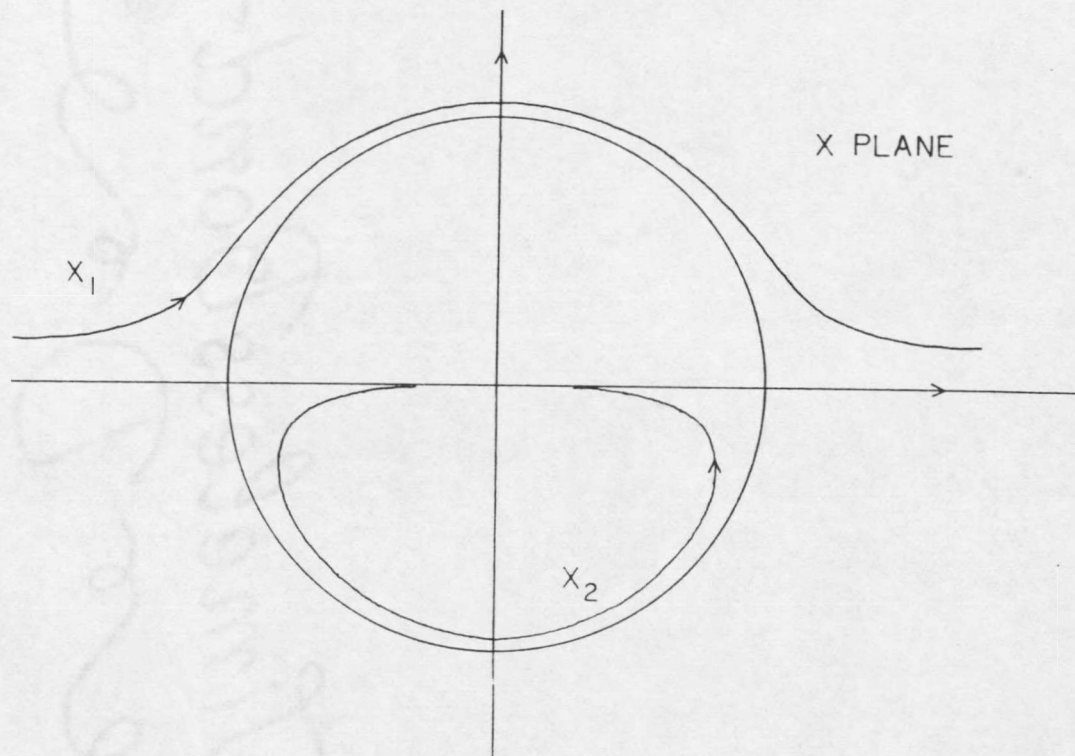


Figure 1. Argand Diagram for One-Band Model.
The arrows indicate increasing energy.

resolvent of H . In this context it may be seen that x_2 is the inter-layer phase of the Bloch solution of energy E , and when E is outside the range of the allowed Bloch-like solutions, then x_2 corresponds to the decrement per layer of the analytically continued Bloch functions which decrease exponentially²¹.

$$G_\ell \sim e^{ik|\ell|a}, \quad |E-\epsilon| < 2\mu, \quad (77)$$

$$G_\ell \sim e^{-\kappa|\ell|a}, \quad |E-\epsilon| > 2\mu.$$

From (68), the expression for G_ℓ is seen to be

$$G_\ell(E) = \frac{x_2^{|\ell|}}{2\mu \sqrt{\left(\frac{E-\epsilon}{2\mu}\right)^2 - 1}} \quad (78)$$

Thus, from (28), the density of states on any bulk layer is

$$D(E) = -\frac{1}{\pi} \text{Im.} \langle \ell | G(E) | \ell \rangle \quad (79)$$

$$= -\frac{1}{\pi} \text{Im.} G_0(E).$$

$$D(E) = \frac{1}{2\pi\mu \sqrt{1 - \left(\frac{E-\epsilon}{2\mu}\right)^2}} \quad (80)$$

Expression (80) holds with the usual meaning of the square root for energies $\epsilon - 2\mu < E < \epsilon + 2\mu$, in the limit that $\eta \rightarrow 0$. If η is left finite, then the inverse square root singularities of (80) are rounded off.

Equation (36) affords an expression for the surface Green function. Region B consists, in the simple model of the present example, of $\ell=0$, while region A consists of $\ell=1,2,3,\dots$.

$$J_{\ell\ell} = G_{\ell-\ell} - G_{\ell-0} G_{0-0}^{-1} G_{0-\ell}. \quad (81)$$

Putting (78) into (81) yields

$$J_{\ell\ell} = \frac{1 - x_2^{2\ell}}{2\mu \sqrt{\left(\frac{E-\epsilon}{2\mu}\right)^2 - 1}} \quad (82)$$

for $\ell=1,2,3,\dots$ and for $E > \epsilon + 2\mu$.

The density of states on the ℓ 'th layer can be obtained from (82) via (28). The square root which appears in the denominator as well as implicitly in x_2 must be analytically continued into the band $|E - \epsilon| < 2\mu$, as it was in expression (79) to obtain formula (80). Also, since from (74) $x_2 \sim e^{ika}$ in this region, the form of the Green function becomes:

$$J_{\ell\ell}(E) = \frac{1 - \cos 2\ell ka - i \sin 2\ell ka}{2i\mu \sqrt{1 - \left(\frac{E-\epsilon}{2\mu}\right)^2}} \quad (83)$$

when $|E - \epsilon| < 2\mu$. Thus, from (28) the density of states on layer ℓ is

$$D_{\ell}(E) = \frac{1 - \cos 2\ell ka}{2\pi\mu \sqrt{1 - \left(\frac{E - \epsilon}{2\mu}\right)^2}} \quad (84)$$

The cosine may be made more agreeable in form by noting that

$$\cos ka = \frac{1}{2}(x_1 + x_2) = \left(\frac{E - \epsilon}{2\mu}\right) \quad (85)$$

Define the ℓ 'th Tchebychev polynomial as

$$T_{\ell}(x) = \cos [\ell \cos^{-1}(x)]. \quad (86)$$

This definition allows the layer density of states on the ℓ 'th layer to be written

$$D_{\ell}(E) = \left\{ 1 - T_{2\ell} \left(\frac{E - \epsilon}{2\mu} \right) \right\} D(E) \quad (87)$$

where $D(E)$ is given by (80).

Both the bulk density of states per layer D and the layer density D_{ℓ} for $\ell=1,2,3$ and 7 are presented in figure 2. Note the way in which the layer density approaches the bulk value²³. This is reminiscent of the way in which the squares of the harmonic oscillator wave functions approach the classical probability distribution as the oscillator quantum number n goes to infinity. The physics here is not closely related to the oscillator case however. The nodes on the layer density of states function on the ℓ 'th layer are caused by the factor $|\langle \ell | \nu \rangle|^2$ which appears in equation (27). The exact eigenstate which is represented by $|\nu\rangle$ is forced to have a node on layer $\ell=0$, i.e., $\langle 0 | \nu \rangle = 0$. $|\nu\rangle$ is thus a standing wave whose wave length depends upon energy. At

