



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

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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.

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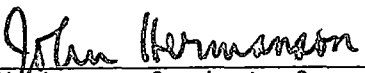
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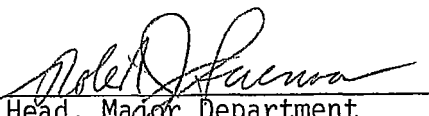
DOCTOR OF PHILOSOPHY

in

PHYSICS

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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.

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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:

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

where U and μ are integrals

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

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

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

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 $a_{\ell'}$ 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

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

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

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

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 .

$$D_j(E) = \sum_v |\langle v | j \rangle|^2 \delta(E-E_v). \tag{25}$$

This would permit evaluation of projected sums of the form

$$\sum_v |\langle j | v \rangle|^2 f(E_v) = \int D_j(E) f(E) dE. \tag{26}$$

As an example, the local density of states

$$D_\ell(E) = \sum_v |\langle \ell | v \rangle|^2 \delta(E-E_v) \tag{27}$$

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

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

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

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

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

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 $R_{\ell'\ell} \equiv J_{\ell'+1, \ell+1}$. 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 $0 < \kappa a < 1$. 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

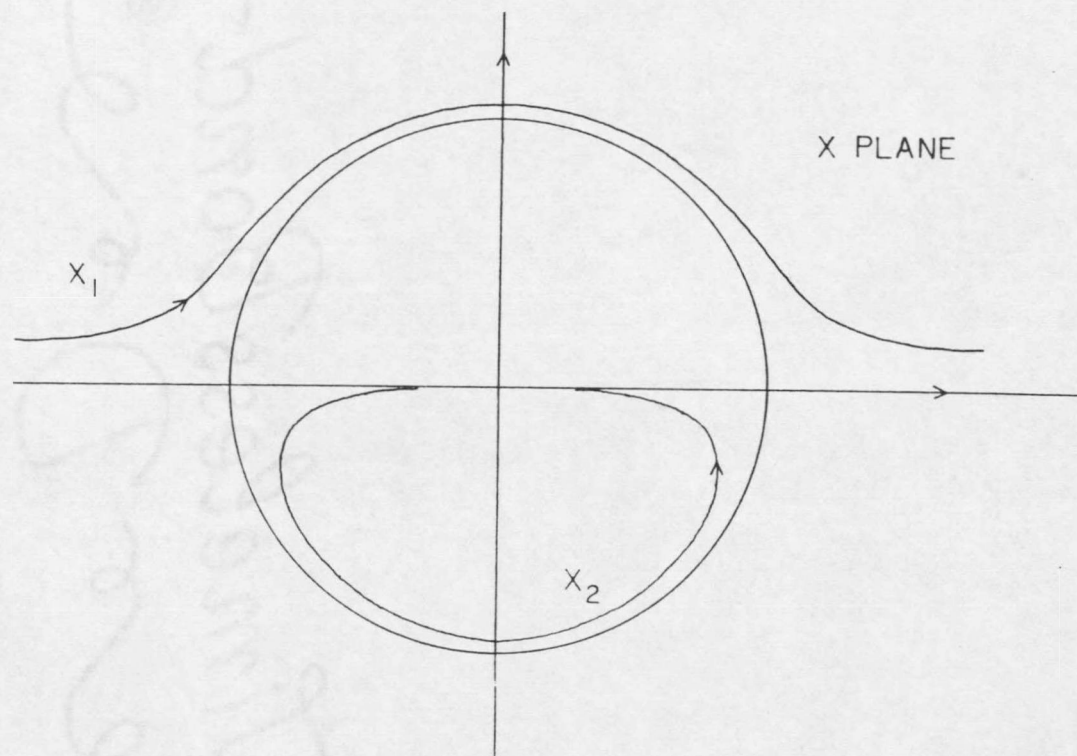


Figure 1. Argand Diagram for One-Band Model.
The arrows indicate increasing energy.

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 $|\langle \ell | v \rangle|^2$ which appears in equation (27). The exact eigenstate which is represented by $|v\rangle$ is forced to have a node on layer $\ell=0$, i.e., $\langle 0 | v \rangle = 0$. $|v\rangle$ is thus a standing wave whose wave length depends upon energy. At

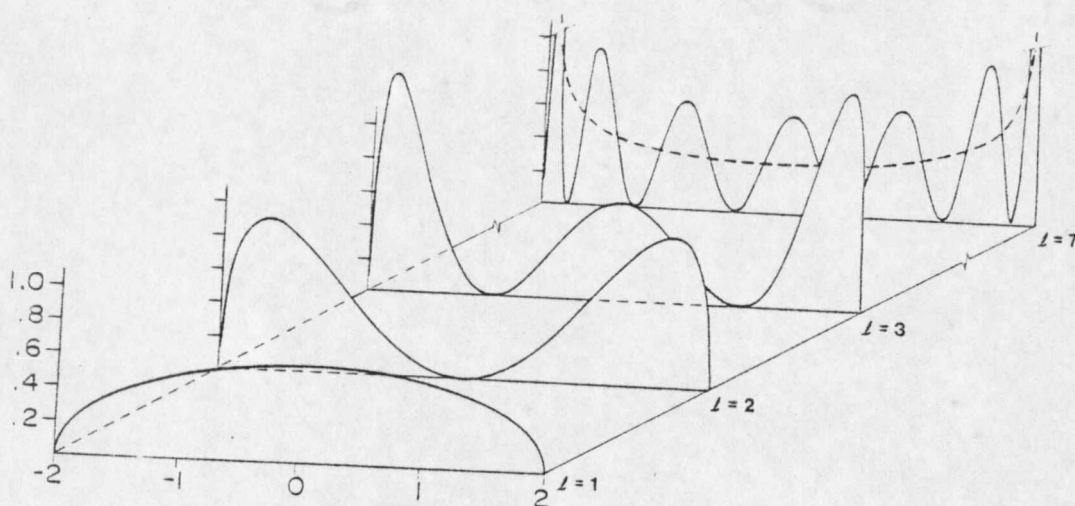


Figure 2. Layer Densities of States for the One-Band Model.

Abcissa is energy in quarter band-width units and the area under each curve is one. The dashed curve shown on layer 7 is the bulk density of states.

certain energies $|\nu\rangle$ will have a node at layer ℓ . Then $\langle \ell | \nu \rangle = 0$ and D_ℓ will have a node at that energy. In this sense, the node structure is a standing wave effect.

It may not be possible to detect the wiggles predicted by this model in the layer density of states by performing an angle resolved photoemission experiment. The reasoning, which is based on the three step model^{24,25} is as follows.

What one might expect to see coming out of the crystal at a given value of k_y and k_z (the surface k-vector) and a given energy E , would be a sum over layers of the initial densities of states on each layer weighted by the probability that an electron on a particular layer, once excited by a photon, can escape. The photocurrent would then be proportional to

$$A(\alpha, E) = \sum_{\ell} D_{\ell}(E) e^{-\alpha \ell} \quad (88)$$

This expression, which vastly oversimplifies the photoemission process, ignores the joint density of states and matrix element effects as well as the surface transmission of the electron and other important aspects of the excitation and detection of the emitted electron. Most of these refinements cannot be computed within the framework of a tight-binding model. The α in (88) is a reciprocal scattering length in units of layer separation. Thus $e^{-\alpha \ell}$ is the escape probability for an electron on layer ℓ . One of the major approximations involved in

(88) is the assumption of incoherence, that is the assumption that the probabilities rather than probability amplitudes add. For this reason $A(\alpha, E)$ might be called an incoherent sum.

The sum $A(\alpha, E)$ of (88) may be most easily evaluated by using the expression (82) for $J_{\ell\ell}$, multiplying by $e^{-\alpha\ell}$ and summing, then in the end taking the imaginary part. The result is

$$A(\alpha, E) = D(E) \left[\frac{1}{1-e^{-\alpha}} - \frac{1-e^{-\alpha} \cos 2ka}{1-2e^{-\alpha} \cos 2ka + e^{-2\alpha}} \right] \quad (89)$$

where

$$\left(\frac{E-\epsilon}{2\mu} \right) = \cos ka.$$

The sum $A(\alpha, E)$ in (89) is seen to have no zeros between the singularities of $D(E)$. The reason for this is closely related to the following power series approximation.

$$\frac{1}{1-p} = 1 + p + p^2 + p^3 + \dots \quad (90)$$

The left hand side of (90) has no zeros in the finite plane while the left hand side, truncated to a polynomial of degree n , has exactly n zeros on the unit circle which become more and more dense as n increases.

Two important limits must obtain from (89). In the limit that the escape depth becomes small and so $\alpha \rightarrow \infty$, $A(\alpha, E)$ must vanish as

$$\lim_{\alpha \rightarrow \infty} A(\alpha, E) \sim D_1(E) e^{-\alpha}. \quad (91)$$

Also, in the limit of long escape depth, $\alpha \rightarrow 0$, $e^{-\alpha} \rightarrow 1$, the incoherent sum must diverge in proportion to the escape depth and approach the shape of the bulk density of states.

$$\lim_{\alpha \rightarrow 0} A(\alpha, E) \sim \frac{1}{\alpha} D(E). \quad (92)$$

Asymptotic property (91) follows from (89) via power series expansion in the variable $e^{-\alpha}$, while (92) follows from expansion of (89) in the variable α . Figure 3 presents the incoherent sum for several different values of α in the case of the simple model problem of this section. The asymptotic properties (91) and (92) are evident as well as is the absence of the nodal structure found in figure 2.

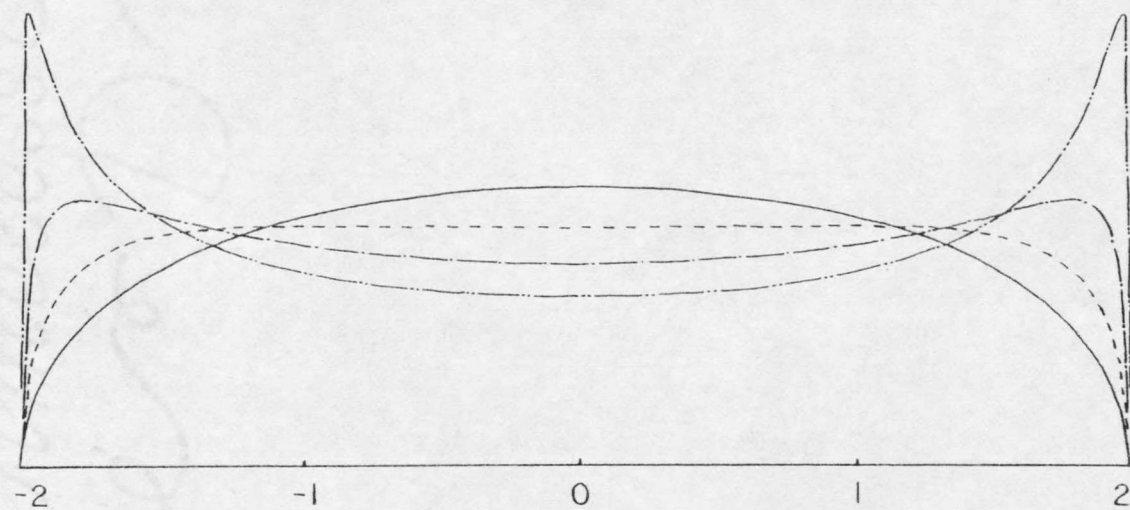


Figure 3. Incoherent Sums for the One-Band Model.

III. TWO-BAND CASE

A. S-P Band, Normal Emission²⁶

1. Bulk. In this section a simple cubic crystal is considered in which there are on each site both s and p-like atomic orbitals. First, layer orbitals are formed exactly as was done in (4).

$$|\alpha, \ell, k_y, k_z\rangle = \frac{1}{N} \sum_{mn} e^{ia(mk_y + nk_z)} |\alpha, \ell, m, n\rangle \quad (93)$$

where α is s, p_x , p_y or p_z .

In the following computation, the restriction $k_y=0$, $k_z=0$ will be made. This restriction would be of interest in the interpretation of an angle resolved photoemission experiment where only those electrons are collected which are emitted normal to the surface. Note that in this s-p model the normal direction is the x-direction, as it was for the simple one-band model. This normal emission case is of interest here for a couple of reasons, both of which involve the rotation symmetry of the surface.

First, because of this symmetry, p_y orbitals on a particular layer will mix only with p_y orbitals on other layers; never with orbitals of other symmetry. Likewise, p_z orbitals mix only with p_z orbitals. Both p_x and s orbitals transform the same way and so they will mix with each other. In other words: The group of the rotation symmetry of the surface and hence of the total Hamiltonian is C_{4v} . p_x and s

transform according to the identity representation. p_y and p_z transform according to different rows of a two-dimensional representation of C_{4v} . All matrix elements of an operator between functions belonging to different irreducible representations or to different rows of the same irreducible representation of its symmetry group must vanish²⁷. Hence, the Hamiltonian, including the surface effect, does not mix them.

Secondly, again because of surface rotation symmetry, there are well-defined selection rules for a given polarization of the incident photon. The reason is that the matrix elements between the initial and final state of the electron-photon coupling term of the Hamiltonian reduce to matrix elements of the momentum operator which is a vector and thus transforms in a particular way under rotation. So by selecting a particular polarization state, the experiment can selectively probe initial states with a particular symmetry. This is especially true because, as Hermanson has shown²⁸, the final state must be even.

The object of the present computation is to obtain layer densities of states in this simple two-band case. From now on the indices k_y and k_z which are both zero, will not appear in the notation. The collection of p_y states and that of p_z states form separate problems which look exactly like the one band model of the previous section, and we consider these problems solved.

The s and p_x states are mixed by the bulk Hamiltonian and the matrix elements between layer orbitals of these states will be defined as follows, assuming only nearest neighbor interactions.

$$\begin{aligned}
 \langle s, \ell' | H^{(0)} | s, \ell \rangle &= \epsilon_s \delta_{\ell', \ell} \\
 &+ \mu_s (\delta_{\ell', \ell+1} + \delta_{\ell', \ell-1}) \\
 \langle s, \ell' | H^{(0)} | p, \ell \rangle &= g (\delta_{\ell', \ell+1} - \delta_{\ell', \ell-1}) \\
 \langle p, \ell' | H^{(0)} | s, \ell \rangle &= -g (\delta_{\ell', \ell+1} - \delta_{\ell', \ell-1}) \\
 \langle p, \ell' | H^{(0)} | p, \ell \rangle &= \epsilon_p \delta_{\ell', \ell} \\
 &+ \mu_p (\delta_{\ell', \ell+1} + \delta_{\ell', \ell-1}).
 \end{aligned} \tag{94}$$

The states used in (94) are related to those defined in (93) by

$$\begin{aligned}
 |s, \ell\rangle &= |s, \ell, k_y=0, k_z=0\rangle, \\
 |p, \ell\rangle &= |p_x, \ell, k_y=0, k_z=0\rangle.
 \end{aligned} \tag{95}$$

As in the one-band case, because of translation symmetry, both $H^{(0)}$ and G are functions only of the layer difference and thus only require one layer subscript.

Define

$$G = \begin{pmatrix} G_{\ell}^{ss} & G_{\ell}^{sp} \\ G_{\ell}^{ps} & G_{\ell}^{pp} \end{pmatrix} \tag{96}$$

The equations of motion follow from (17)

$$(E - H^{(0)})G = 1 \quad (97)$$

Thus

$$-H_{+1}^{(0)}G_{\ell-1} + (1E - H_0^{(0)})G_{\ell} - H_{-1}^{(0)}G_{\ell+1} = 1\delta_{\ell 0} \quad (98)$$

where

$$H_{-1}^{(0)} = H_{+1}^{(0)T} = \begin{pmatrix} \mu_s & g \\ -g & \mu_p \end{pmatrix} \quad (99)$$

(T means transpose),

$$H_0^{(0)} = \begin{pmatrix} \epsilon_s & 0 \\ 0 & \epsilon_p \end{pmatrix} \quad (100)$$

and

$$1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (101)$$

Expression (98) represents a set of coupled, second order, linear difference equations with constant coefficients. They will be solved by the method of generating functions.

Define a 2x2 matrix generating function

$$F(s, E) = \sum_{\ell} s^{\ell} G_{\ell}(E) \quad (102)$$

Using (102) in (98) gives

$$-sH_{+1}^{(0)}F + (1E - H_0^{(0)})F - \frac{1}{s}H_{-1}^{(0)}F = 1. \quad (103)$$

Thus

$$\begin{aligned}
F^{-1} &= (1E - H_0^{(0)} - sH_{+1}^{(0)} - \frac{1}{s} H_{-1}^{(0)}) \\
&= \begin{pmatrix} (E - \epsilon_s) - \mu_s(s + \frac{1}{s}) & g(s - \frac{1}{s}) \\ -g(s - \frac{1}{s}) & (E - \epsilon_p) - \mu_p(s + \frac{1}{s}) \end{pmatrix}.
\end{aligned} \tag{104}$$

An important ingredient required for the inversion of F^{-1} in order to produce F is the determinant of F^{-1} .

$$\begin{aligned}
\Delta(s, E) = \det F^{-1} &= (E - \epsilon_s)(E - \epsilon_p) - [\mu_s(E - \epsilon_p) + \mu_p(E - \epsilon_s)](s + \frac{1}{s}) \\
&\quad + \mu_s \mu_p (s + \frac{1}{s})^2 + g^2 (s - \frac{1}{s})^2.
\end{aligned} \tag{105}$$

The analytic singularity structures of F and thus of G_ℓ , are determined by the zeros of Δ . Δ is the Fredholm determinant corresponding to the bulk Hamiltonian²⁹; it contains the dispersion formulas for the bulk band states, as will be shown in the following consideration.

Exactly as in the one band case, the zeros of Δ represent solutions of the homogeneous eigenvalue problem (76) for the bulk Hamiltonian. In the case when E is inside a continuum of $H^{(0)}$, s is of the form

$$s = e^{ika} \tag{106}$$

where k is a real wave number, as is x_2 in (74). Using this in (105), the zeros of $\Delta(e^{ika}, E)$ are found to occur when E takes on one of two values

$$E^{\pm}(k) = \frac{1}{2}[\epsilon_s + \epsilon_p + 2(\mu_s + \mu_p)\cos ka] \quad (107)$$

$$\pm \sqrt{[\epsilon_s - \epsilon_p + 2(\mu_s - \mu_p)\cos ka]^2 + 16g^2 \sin^2 ka}.$$

The notation may be simplified if energy is measured with respect to ϵ_s and in units of $|\mu_s|$. Then,

$$\begin{aligned} \epsilon_s &\rightarrow 0 & \mu_s &\rightarrow -1 \\ \epsilon_p &\rightarrow \epsilon & \mu_p &\rightarrow \mu \end{aligned} \quad (108)$$

The reason for choosing μ_s to be -1 rather than 1 is that this causes the s-band to bend up rather than down. The explicit relation between the new symbols and the old which is implied by (108) is

$$\begin{aligned} \epsilon &= \frac{\epsilon_p - \epsilon_s}{|\mu_s|} \\ \mu &= \mu_p / |\mu_s|. \end{aligned} \quad (109)$$

The energy parameter is now

$$\omega = \frac{E - \epsilon_s}{|\mu_s|}, \quad (110)$$

The expression (107) for the band energies has become in these parameters

$$\omega_{\pm}(k) = \frac{1}{2}\epsilon + (\mu - 1)\cos ka \pm \frac{1}{2}\sqrt{[\epsilon + 2(\mu + 1)\cos ka]^2 + 16g^2 \sin^2 ka}. \quad (111)$$

The band structure for this two band model in the direction

perpendicular to the (100) surface, as prescribed by equation (111), is presented in figure 4. The choice of μ , ϵ and g in figure 4 is $\mu=.2$, $\epsilon=1$, $g=.1$. For other choices of these parameters, the bands may look even qualitatively different. The existence of a gap and hence of a gap surface state depends upon the relative values of μ , ϵ and g ^{18,23,30}. The values of energy for which the slope of the ω versus ka curve is zero represent van Hove singularities in the bulk density of states function. As we have seen in the one band case, the van Hove singularities represent branch points in the dispersion formulas and are the points which delimit the continua of the spectrum of the bulk Hamiltonian operator.

The form of the determinant Δ is now

$$\Delta(s, \omega) = \frac{g^2 - \mu}{s^2} p(s, \omega), \quad (112)$$

where p is a monic polynomial

$$p(s) = s^4 - Qs^3 + (R+2)s^2 - Qs + 1 \quad (113)$$

$$\text{with } Q(\omega) = \frac{(\mu-1)\omega+\epsilon}{g^2-\mu} \quad (114)$$

$$\text{and } R(\omega) = \frac{\omega(\omega-\epsilon)}{g^2-\mu} - \frac{4g^2}{g^2-\mu}. \quad (115)$$

This polynomial has reciprocal symmetry. If s_0 is a root of p , then $1/s_0$ is also a root. Thus, p may be factored

$$p(s) = (s^2 + \alpha s + 1)(s^2 + \beta s + 1) \quad (116)$$

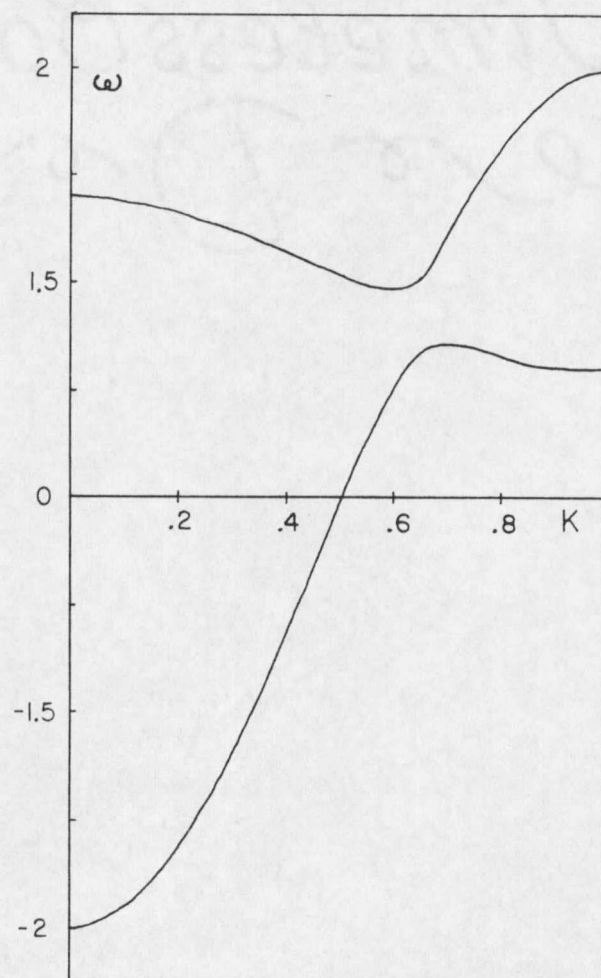


Figure 4. Bands for the s-p Model.

K is wave number in units of $\frac{\pi}{a}$.

Multiplication shows that

$$\begin{aligned}\alpha + \beta &= -Q \\ \alpha\beta + 2 &= R + 2\end{aligned}\tag{117}$$

Thus α and β are the zeros of

$$y^2 + Qy + R\tag{118}$$

In other words,

$$\begin{aligned}\alpha &= -\frac{1}{2}Q + \frac{1}{2}\sqrt{D} \\ \beta &= -\frac{1}{2}Q - \frac{1}{2}\sqrt{D},\end{aligned}\tag{119}$$

where D is the discriminant

$$D = Q^2 - 4R\tag{120}$$

In order to forestall the eventual computational catastrophe, beyond which the algebraic complexity of the solution may obscure the physical meaning, it is important at this point to catalogue a number of relations among the roots of the reduced, quadratic equation of (118).

$$\begin{aligned}\alpha + \beta &= Q \\ \alpha\beta &= R \\ \alpha - \beta &= \sqrt{D} = \sqrt{Q^2 - 4R}\end{aligned}\tag{121}$$

Also, there is a reduced, homogeneous difference equation satisfied by powers of α and β .

$$\alpha^n = -Q\alpha^{n-1} - R\alpha^{n-2}\tag{122}$$

$$\beta^n = - Q\beta^{n-1} - R\beta^{n-1}.$$

Next, the singularities of D must be examined. From the definition (120), it follows that

$$D(\omega) = \frac{(\mu+1)^2 - 4g^2}{(g^2 - \mu)^2} [\omega^2 - 2a\omega + b], \quad (123)$$

where

$$a = \epsilon \left(\frac{(\mu+1) - 2g^2}{(\mu+1)^2 - 4g^2} \right) \quad (124)$$

and

$$b = \frac{\epsilon^2 + 16g^2(g^2 - \mu)}{(\mu+1)^2 - 4g^2}. \quad (125)$$

The roots in ω of the polynomial D are the positions of the van Hove singularities which delimit the s-p hybridization gap which is manifest in the expression for the bands (111), and is demonstrated in figure 4. The existence of such a gap depends upon the reality in ω of the roots of D. Thus we examine the points where the nature of these roots changes. The discriminant of the roots of D (a discriminant of a discriminant) is

$$d = a^2 - b \quad (126)$$

We consider zeros of

$$[(\mu+1)^2 - 4g^2](a^2 - b) = 0 \quad (127)$$

under the supposition that the first factor is not identically zero.

$$[(\mu+1)^2 - 4g^2](a^2-b) = 4g^2\{16g^4 + [\epsilon^2 - 4(\mu+1)^2 - 16\mu]g^2 + [4\mu(\mu+1)^2 - \epsilon^2\mu]\}. \quad (128)$$

Thus the zeros of D, which depend upon expression (128) are given by

$$\omega_{\pm} = \frac{[(\mu+1) - 2g^2]\epsilon \pm 2g\sqrt{\rho}}{(\mu+1)^2 - 4g^2} \quad (129)$$

The function ρ in (129) is given as

$$\rho(g^2, \epsilon, \mu) = 16g^2 + [\epsilon^2 - 4(\mu+1)^2 - 16]g^2 + [4\mu(\mu+1)^2 - \epsilon^2\mu]. \quad (130)$$

The center of the hybridization gap is

$$\text{gap center} = \frac{[(\mu+1) - 2g^2]\epsilon}{[(\mu+1)^2 - 4g^2]}, \quad (131)$$

and the width

$$\text{gap width} = \frac{4g\sqrt{\rho(g^2, \epsilon, \mu)}}{(\mu+1)^2 - 4g^2} \quad (132)$$

It is reasonable to assume that $4g^2 < (\mu+1)^2$. Under this assumption, the complex square root of D according to the branch convention

$$D = \frac{\sqrt{(\mu+1)^2 - 4g^2}}{g^2 - \mu} \sqrt{\omega - \omega_+} \sqrt{\omega - \omega_-} \quad (133)$$

Next, the zeros of p defined in (113) must be computed using

$$s^2 + \alpha s + 1 = 0 \quad (134)$$

$$s^2 + \beta s + 1 = 0,$$

or

$$s_{1,2} = -\frac{1}{2}\alpha \pm \frac{1}{2}\sqrt{\alpha^2 - 4} \quad (135)$$

$$s_{3,4} = -\frac{1}{2}\beta \pm \frac{1}{2}\sqrt{\beta^2 - 4}$$

The following properties among the roots (135) are of considerable importance:

$$s_1 + s_2 = \alpha, \quad s_3 + s_4 = \beta \quad (136)$$

$$s_1 s_2 = 1, \quad s_3 s_4 = 1 \quad (137)$$

$$s_1 - s_2 = \sqrt{\alpha^2 - 4} \quad s_3 - s_4 = \sqrt{\beta^2 - 4} \quad (138)$$

Now the branch point singularities of the root expression must be explored and must ultimately relate to van Hove singularities in the spectrum of the bulk Hamiltonian $H^{(0)}$.

s_1 and s_2 show branch points when $\alpha = \pm 2$. $\alpha = +2$ implies that either $\omega = 2$, or $\omega = \epsilon - 2\mu$, while $\alpha = -2$ correlates with $\omega = -2$ and $\omega = \epsilon + 2\mu$. These are the band singularities at $ka = \pm \pi$ and at $ka = 0$ respectively. The existence and position in ω of these singularities are not affected by the hybridization strength parameter g , and are the outer limits of the s and p continua in the case $g = 0$ (see figure 4).

s_3 and s_4 have similar branch points at $\beta = \pm 2$. These points are the same as those for which $\alpha = \pm 2$.

In order to understand the paths of the roots s_1, s_2, s_3 and s_4 as they move around the Argand diagram of figure 5 as a function of ω , it

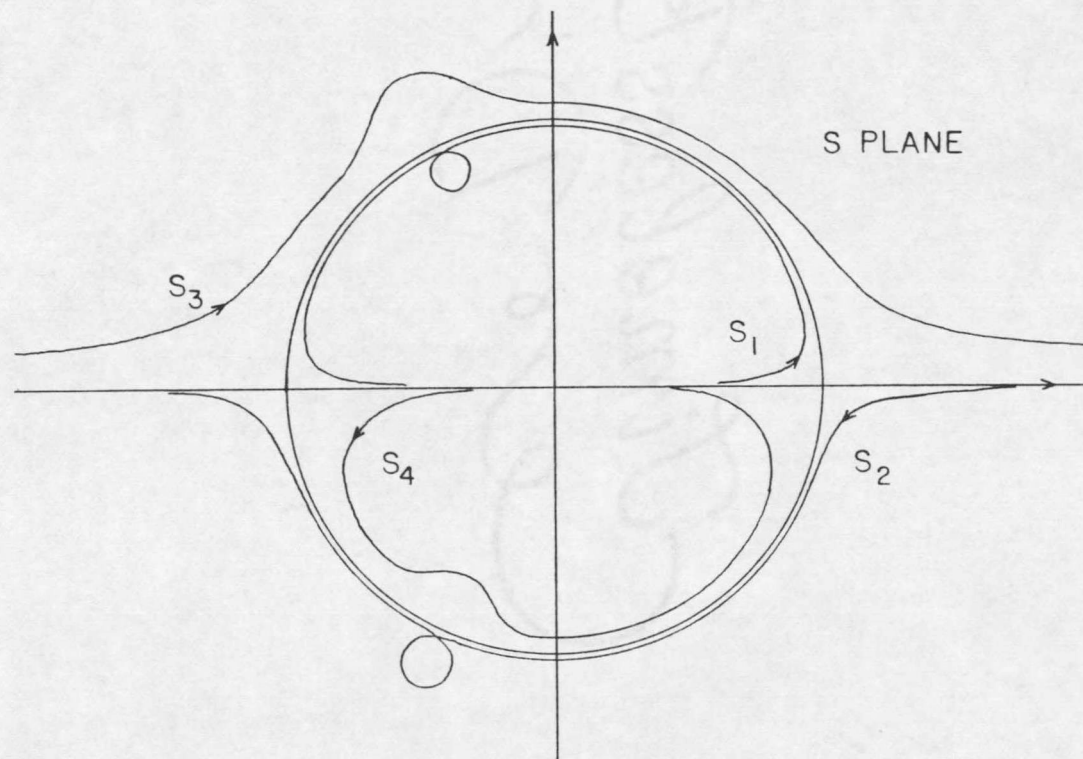


Figure 5. Root Trajectories of a Model Two-Band Hamiltonian.

is convenient to begin with $\omega \gg 2$ and assume $0 < g < \mu < \epsilon < 2$. Then β is negative and α is positive. Thus at this energy, the roots are all real and

$$s_2 < -1 < s_1 < 0 < s_4 < 1 < s_3. \quad (139)$$

As ω becomes less than 2 (with a small, positive imaginary part), then roots s_1 and s_2 leave the real axis and approach the unit circle. s_1 remains inside and s_2 outside. This motion of s_1 and s_2 has an explanation in terms of figure 4. For energy just less than 2 in figure 4, there is a propagating Bloch state of essentially s-like character. The interlayer phase of this state is s_2 , and the value of ka corresponds to the polar angle of s_2 on the Argand plot. s_1 and s_2 would be the Bloch solutions for the s-like part of the Hamiltonian $H^{(0)}$ in the limit that $g \rightarrow 0$. As ω is lowered until $\omega_+ < \omega < \epsilon + 2\mu$, the poles s_3 and s_4 approach the unit circle and represent p-like Bloch states.

The next features of the root trajectories to be considered are the kinks. The loops and bumps which appear in figure 5 have a very interesting significance. For ω values corresponding to the gap (see figure 4) there are no propagating Bloch states. The analytically continued Bloch states are damped, and thus in this region s_1 and s_4 shrink, in magnitude, away from the unit circle. As ω goes below ω_+ , s_1 and s_2 leave the unit circle at a value of polar angle corresponding in the band diagram to the position along ka of the gap center. s_1 and s_2 execute loops in the attenuation region and when ω reaches

ω_- , the roots again return to the unit circle at exactly the same value of ka , thus closing the loops. Regarded as a function of ka , then, figure 4 may be considered as a superposition of two monotonic but discontinuous functions. Therefore the roots s_1 and s_4 , which are roots of the characteristic polynomial of $H^{(0)}$, can be classified according to atomic type even when $g \neq 0$. s_1 is an s-like contribution to G_ℓ , while s_4 is p-like.

At the energies where the kinks appear in the root loci, the continued Bloch functions are exponentially damped and will provide a basis set with which localized surface states may be expanded.

Finally, as ω goes below $\epsilon - 2\mu$, s_3 and s_4 leave the unit circle and then s_1 and s_2 leave at $\omega = -2$.

In order to make the roots continuous functions of ω , the following branch convention has been used:

$$\begin{aligned}\sqrt{\alpha^2 - 4} &= \sqrt{\alpha^2 - 2} \sqrt{\alpha + 2}, \\ \sqrt{\beta^2 - 4} &= \sqrt{-\beta - 2} \sqrt{-\beta + 2},\end{aligned}\tag{140}$$

together with (135) for $\sqrt{D}$. Thus the roots are continuous functions of continuous functions of ω when ω is real except for a small, positive imaginary part.

Returning now to the problem of expanding the generating function in order to obtain the Green functions, we find that

$$F^{ij}(s, \omega) = \frac{\Delta_{ji}(s, \omega)}{\Delta(s, \omega)}, \quad (141)$$

i and j being the states s or p and $\Delta_{ji}(s, \omega)$ representing a cofactor.

Using (112)

$$F^{ij}(s, \omega) = \frac{s^2 \Delta_{ji}(s, \omega)}{(g^2 - \mu)p(s, \omega)}. \quad (142)$$

Thus F^{ij} is a rational function of s with the property that F^{ij} goes to zero at zero and infinity. Also, because of the small positive imaginary part of ω , the poles of F^{ij} are always separated, whence

$$F^{ij}(s, \omega) = \frac{1}{g^2 - \mu} \sum_{k=1}^4 \frac{s_k^2 \Delta_{ij}(s_k, \omega)}{p'(s_k)(s - s_k)}. \quad (143)$$

The various parts of (143) are quite simply computed, using the tools that have been noted in (121), (136), (137) and (138). From (104), the cofactors are

$$\Delta_{ss} = (\omega - \epsilon) - (s + \frac{1}{s}) \quad (144)$$

$$\Delta_{sp} = -g(s - \frac{1}{s}) \quad (145)$$

$$\Delta_{ps} = g(s - \frac{1}{s}) \quad (146)$$

$$\Delta_{pp} = \omega + (s + \frac{1}{s}). \quad (147)$$

The preparation of $G_{\ell}^{ss}(\omega)$ for example, is as follows.

$$s_1^2 \Delta_{ss}(s_1, \omega) = (E - \epsilon) s_1^2 - \mu(s_1^2 + 1) s_1 = (E - \epsilon + \mu\alpha) s_1^2. \quad (148)$$

Similar results follow in the case of s_2 , s_3 , and s_4 . The derivative is computed by factoring $p(s)$.

$$p(s) = (s-s_1)(s-s_2)(s-s_3)(s-s_4) \quad (149)$$

$$p'(s_1) = (s_1-s_2)(s_1-s_3)(s_1-s_4) + 0. \quad (150)$$

Using properties of the roots,

$$p'(s_1) = \sqrt{\alpha^2 - 4} (s_1^2 + \beta s_1 + 1), \quad (151)$$

but $s^2 = -\alpha s_1 - 1$, so

$$p'(s_1) = \sqrt{\alpha^2 - 4} (\beta - \alpha) s_1. \quad (152)$$

Finally from (121), $(\alpha - \beta) = D$.

$$p'(s_1) = -\sqrt{D} \sqrt{\alpha^2 - 4} s_1. \quad (153)$$

Results similar to (153) also hold for the other roots.

Applying the above results to (143) yields

$$\begin{aligned} F^{ss} = & \frac{1}{g^2 - \mu} \frac{1}{\sqrt{D}} \frac{E - \epsilon + \mu\alpha}{\sqrt{\alpha^2 - 4}} \frac{s_2}{s - s_2} - \frac{s_1}{s - s_1} \\ & + \frac{E - \epsilon + \mu\beta}{\sqrt{\beta^2 - 4}} \frac{s_3}{s - s_3} - \frac{s_4}{s - s_4} \end{aligned} \quad (154)$$

The choice of annulus for the expansions of the terms of (154) depends upon the asymptotic form of G_ℓ by an argument similar to that which

follows (70).

$$(s-s_1)^{-1} = (1/s)(1 + s_1/s + s_1^2/s^2 + \dots) \quad (155)$$

$$(s-s_2)^{-1} = -s_1(1 + s_1 s + s_1^2 s^2 + \dots)$$

$$(s-s_3)^{-1} = -s_4(1 + s_4 s + s_4^2 s^2 + \dots)$$

$$(s-s_4)^{-1} = (1/s)(1 + s_4/s + s_4^2/s^2 + \dots)$$

Thus G_ℓ^{SS} is given by

$$G_\ell^{SS} = \frac{1}{(\mu-g^2) \sqrt{D}} \left[\frac{(\omega-\epsilon+\mu\alpha)}{\sqrt{\alpha^2-4}} s_1^{|\ell|} + \frac{(\omega-\epsilon+\mu\beta)}{\sqrt{\beta^2-4}} s_4^{|\ell|} \right]. \quad (156)$$

G_ℓ^{pp} follows from (156) through the replacements $\epsilon = 0$, $\mu = -1$.

$$G_\ell^{pp} = \frac{1}{(\mu-g^2) \sqrt{D}} \left[\frac{(\omega+\alpha)}{\sqrt{\alpha^2-4}} s_1^{|\ell|} + \frac{(\omega+\beta)}{\sqrt{\beta^2-4}} s_4^{|\ell|} \right]. \quad (157)$$

A similar computation produces

$$G_\ell^{Sp} = \frac{g \text{sign}(\ell)}{(\mu-g^2) \sqrt{D}} [s_1^{|\ell|} - s_4^{|\ell|}], \quad (158)$$

$$\text{and } G_\ell^{ps} = -G_\ell^{Sp}. \quad (159)$$

The bulk densities of states which follow from (156) and (157) are presented in figure 6. The total density of states on a bulk layer is the sum of two contributions.

$$D(\omega) = D^S(\omega) + D^P(\omega) \quad (160)$$

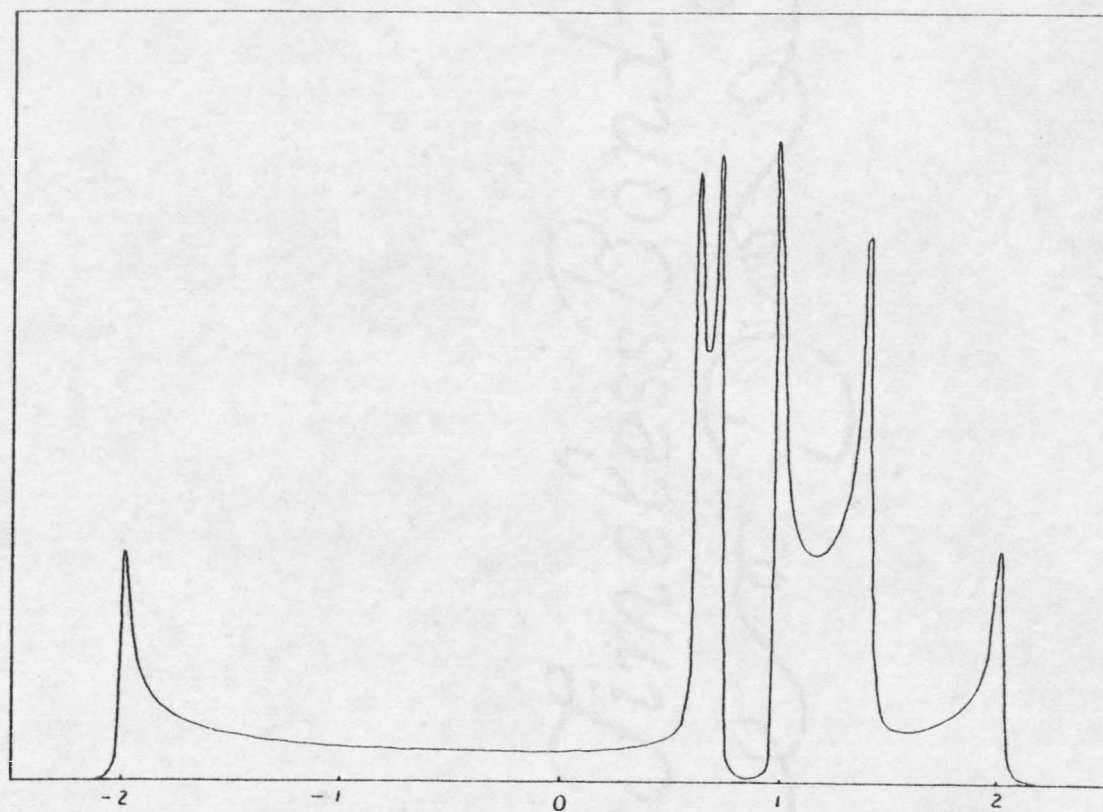


Figure 6. Total Bulk Density of States per Layer for the s-p Model. The energy axis is in quarter s-band units. The area under the curve is two.

It is a characteristic of the resolvent method that the densities of states occur naturally in component form. The densities D^S and D^P of figure 6 are computed from

$$D^i(\omega) = -\frac{1}{\pi} \text{Im } G_0^{ii}(\omega) \quad (161)$$

where i is either s or p .

2. Surface. The surface problem may now be solved using (26).

$$J_{\ell\ell}^{ii} = G_{\ell=0}^{ii} - \sum_{\substack{j=s,p \\ k=s,p}} G_{\ell}^{ij} (G_0^{-1})^{jk} G_{-\ell}^{ki} \quad (162)$$

There is a possibility that this function may have a pole when the determinant of G_0 has a zero. From (156-159), the form of G_0 is:

$$G_0 = \frac{1}{(\mu - g^2) \sqrt{D}} \begin{pmatrix} u & 0 \\ 0 & v \end{pmatrix}. \quad (163)$$

The functions u and v are

$$u = \frac{(\omega - \epsilon + \mu\alpha)}{\sqrt{\alpha^2 - 4}} - \frac{(\omega - \epsilon + \mu\beta)}{\sqrt{\beta^2 - 4}} \quad (164)$$

$$v = \frac{\omega + \alpha}{\sqrt{\alpha^2 - 4}} + \frac{\omega + \beta}{\sqrt{\beta^2 - 4}}.$$

Zeros of u and v define the zeros of the determinant and hence determine the poles of $J_{\ell\ell}$. The zeros of u occur at the points $\omega = \pm 2$, the s -band edges, and at $\omega = \frac{\epsilon}{\mu+1}$, which is the point at which the separate s and p -bands would have crossed if the mixing parameter g were set to

zero. See (111). On the other hand, the zeros of v are at $\omega = \epsilon \pm 2\mu$, the p-band edges, and again at the crossing point $\omega = \frac{\epsilon}{\mu+1}$. It may be seen from (162) that the zeros at the band edges will not cause poles because these will be cancelled by other zeros in the numerators. But there will always exist an isolated surface state in such a gap exactly at the energy where the bands would have crossed if there were no s-p mixing^{18,30}.

Figure 7 illustrates the densities of states curves on layers near the surface for the s-p model in normal photoemission. Noteworthy features in figure 7 include the state in the s-p hybridization gap, the appearance of standing-wave nodal structures similar to that observed in the one-band model²³, and the softening of the bulk singularities on the layers near the surface⁷. The singularities in the bulk densities are of the reciprocal square root type, while those near the surface are softened to square root shoulders. These features are rather typical of the kinds of effects produced in tight-binding models with more realistic Hamiltonians^{7,8}.

B. Simple Bond-Orbital Model

1. Bulk. A number of simplifications have been proposed for the treatment of semiconductor surface states which would allow a reasonably realistic description of the Hamiltonian and yet keep the computation as simple as possible.

Harrison³¹ has proposed a very simple model Hamiltonian which

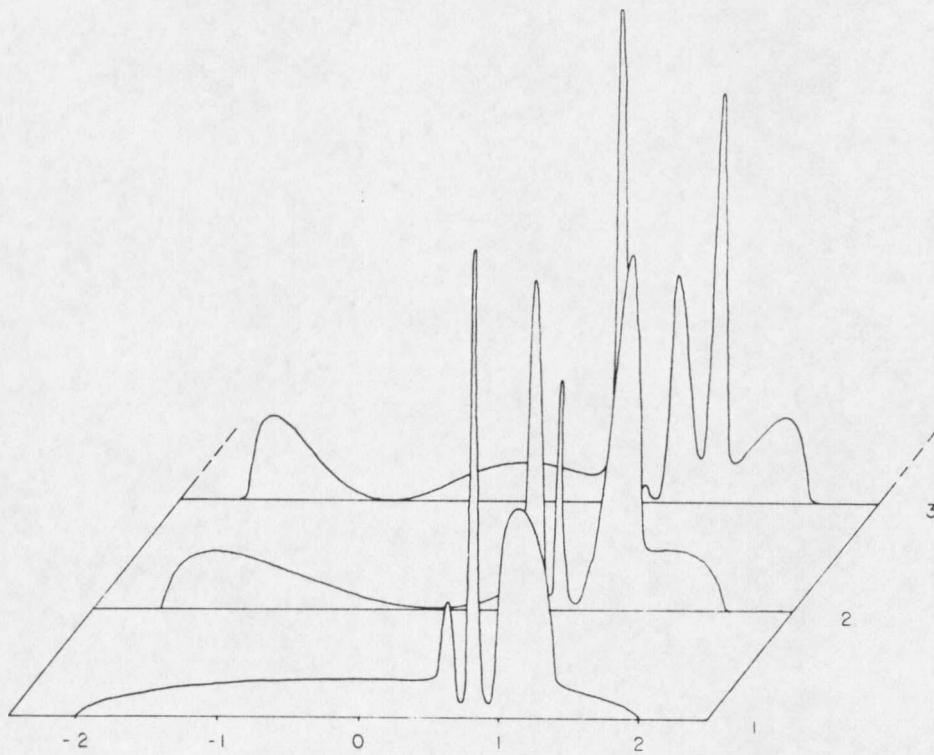


Figure 7. Total Layer Densities of States for the s-p Model on Layers 1, 2 and 3. Energy is in quarter s-band units.

reproduces many of the bulk properties of a large class of semiconductors. Recently, several authors ³²⁻³⁴ have applied Harrison's bond-orbital model to surface state computation. This will be done here also. In the present section, a bond-orbital will be developed as a simplification to the two-band model of the previous discussion. The brief treatment below is offered as an introduction to the more elaborate bond-orbital model of the next section.

Figure 8 illustrates various steps in the calculation of chemical bonding for a simple diatomic molecule. In figure 8a shows s and p states on two isolated atoms. Let $|s1\rangle$, $|p1\rangle$ be s and p states centered on site 1 and let $|s2\rangle$ and $|p2\rangle$ be the same states centered on site 2.

As the two atoms are brought together, the interaction between them is represented in terms of Hamiltonian matrix elements between the orbitals.

$$\langle s1|H|s1\rangle = \langle s2|H|s2\rangle = \epsilon_s \quad (165)$$

$$\langle p1|H|p1\rangle = \langle p2|H|p2\rangle = \epsilon_p$$

$$\langle s1|H|s2\rangle = \langle s2|H|s1\rangle = \mu_s$$

$$\langle p1|H|p2\rangle = \langle p2|H|p1\rangle = \mu_p$$

$$\langle s1|H|p2\rangle = \langle p2|H|s1\rangle = g$$

$$\langle s2|H|p1\rangle = \langle p1|H|s2\rangle = -g$$

Assume all other matrix elements are zero. Ignore electron-electron repulsion and other effects and also assume that the overlap between

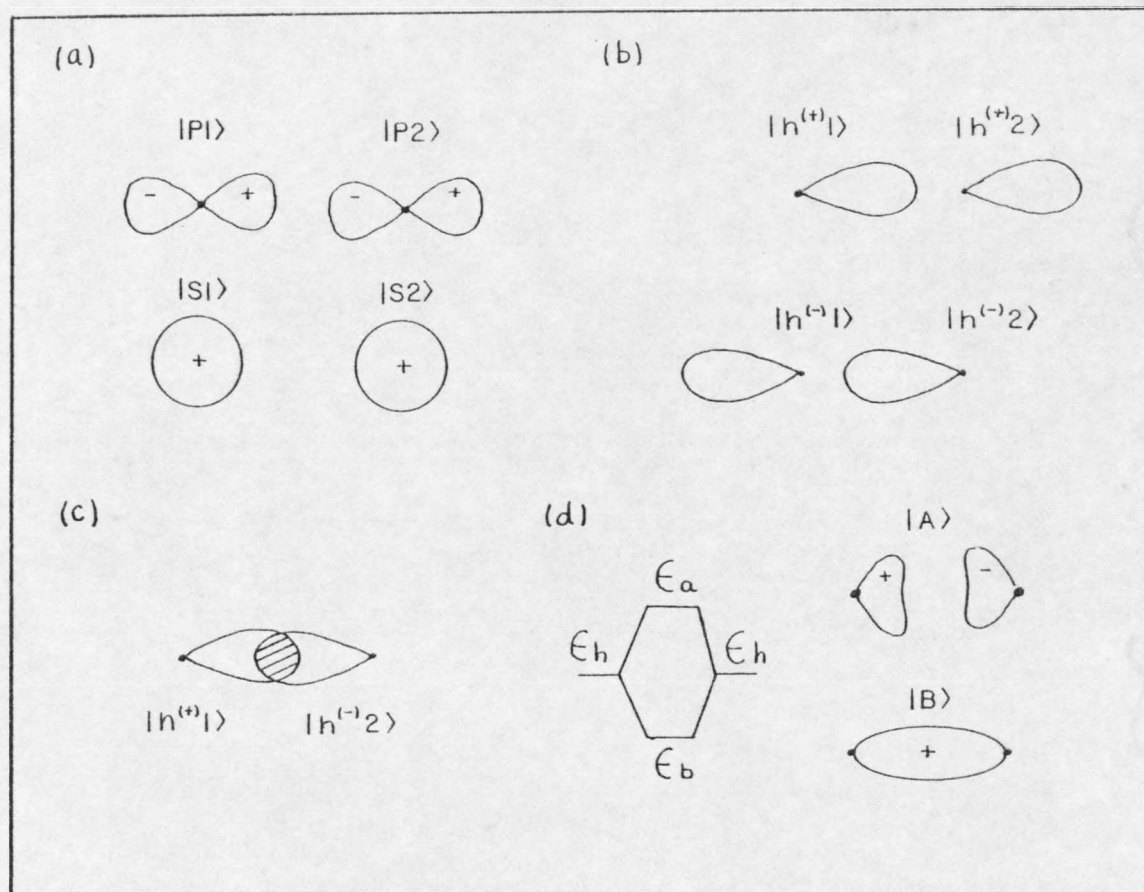


Figure 8. Formation of a Chemical Bond.

orbitals vanishes.

Figure 8b represents a hybrid basis set formed from linear combinations of the s and p orbitals on the two atoms.

$$|h^{(+)}_1\rangle = \frac{1}{2}(|s_1\rangle + |p_1\rangle) \quad (166)$$

$$|h^{(-)}_1\rangle = \frac{1}{2}(|s_1\rangle - |p_1\rangle)$$

$$|h^{(+)}_2\rangle = \frac{1}{2}(|s_2\rangle + |p_2\rangle)$$

$$|h^{(-)}_2\rangle = \frac{1}{2}(|s_2\rangle - |p_2\rangle) .$$

As the atoms come together, as illustrated in 8c, the hybrid orbitals $|h^{(+)}_1\rangle$ and $|h^{(-)}_2\rangle$ interact strongly and the corresponding energy levels split as shown in figure 8d to form a bonding and an antibonding level. These energy levels belong to a bond-orbital which is the even combination of the two hybrids, and an antibond-orbital, which is the odd combination.

If the original orbitals on the two sites were only half filled with electrons, then those electrons would now occupy the bond-orbital and part of the other hybrid orbitals pointing the other way (non-bonding), but the antibond-orbital would be empty. In this way, the total energy is lowered and a stable bond is formed.

Suppose a crystal were formed from an ensemble of molecules of this simple type. All of the hybrid orbitals would participate in bonding and so there would be no non-bonding levels. In the case

that the broadening of the filled bond-orbitals which now form the valence band does not mix the bonding and antibonding states very strongly compared to the mixing of the bond-orbitals among themselves, then one might hope to represent the valence band as some linear combination of bond-orbitals only and neglect the antibond-orbitals altogether. This is the philosophy adopted when a bond-orbital Hamiltonian is used to represent the valence bands of semi-conductors.

The s-p Hamiltonian used in the two-band calculation may be transformed into bond and antibond-orbitals as follows.

$$\begin{aligned}
 |b, \ell\rangle &= \frac{1}{2}(|h^{(+)}_{\ell}\rangle + |h^{(-)}_{\ell+1}\rangle) \\
 &= \frac{1}{2}(|s, \ell\rangle + |p, \ell\rangle + |s, \ell+1\rangle - |p, \ell+1\rangle) \\
 &= \text{bond orbital near layer } \ell.
 \end{aligned} \tag{166a}$$

$$\begin{aligned}
 |a, \ell\rangle &= \frac{1}{2}(|h^{(+)}_{\ell}\rangle - |h^{(-)}_{\ell+1}\rangle) \\
 &= \frac{1}{2}(|s, \ell\rangle + |p, \ell\rangle - |s, \ell+1\rangle + |p, \ell+1\rangle) \\
 &= \text{antibond-orbital near } \ell.
 \end{aligned}$$

Using the definitions (94) the matrix elements become

$$\begin{aligned}
 \langle b\ell' | H | b\ell \rangle &= \\
 &[\frac{1}{4}(\mu_s + \mu_p) - \frac{1}{2}g]\delta_{\ell', \ell+2} \\
 &+ [\frac{1}{2}(\mu_s + \mu_p) + \frac{1}{4}(\epsilon_s - \epsilon_p)]\delta_{\ell', \ell+1} \\
 &+ [\frac{1}{2}(\epsilon_s + \epsilon_p) + \frac{1}{2}(\mu_s - \mu_p) + g]\delta_{\ell', \ell} \\
 &+ [\frac{1}{2}(\mu_s + \mu_p) + \frac{1}{4}(\epsilon_s - \epsilon_p)]\delta_{\ell', \ell-1}
 \end{aligned} \tag{167}$$

$$+ [\frac{1}{4}(\mu_s + \mu_p) - \frac{1}{2}g] \delta_{l', l-2}$$

$$\langle b_{l'} | H | a_l \rangle =$$

$$[\frac{1}{4}(\mu_p - \mu_s) + \frac{1}{2}g] \delta_{l', l+2}$$

$$+ [\frac{1}{4}(\epsilon_p - \epsilon_s)] \delta_{l', l+1}$$

$$+ [\frac{1}{4}(\epsilon_s - \epsilon_p)] \delta_{l', l-1}$$

$$+ [\frac{1}{4}(\mu_s - \mu_p) - \frac{1}{2}g] \delta_{l', l-2}$$

$$\langle a_{l'} | H | a_l \rangle =$$

$$[\frac{1}{2}(\mu_p - \mu_s) + \frac{1}{2}g] \delta_{l', l+2}$$

$$+ [\frac{1}{2}(\mu_s + \mu_p) + \frac{1}{2}(\epsilon_p - \epsilon_s)] \delta_{l', l+1}$$

$$+ [\frac{1}{2}(\epsilon_s + \epsilon_p) + \frac{1}{2}(\mu_p - \mu_s) - g] \delta_{l', l}$$

$$+ [\frac{1}{2}(\mu_s + \mu_p) + \frac{1}{4}(\epsilon_p - \epsilon_s)] \delta_{l', l-1}$$

$$+ [\frac{1}{2}(\mu_p - \mu_s) + \frac{1}{2}g] \delta_{l', l-2}$$

Two things should be noted about the Hamiltonian defined in (167). First, it represents the same physical situation as does (94) and so both the band structure and the total bulk and surface densities of states would be the same. Second, the range of the interaction has been extended. A Hamiltonian which is nearest-neighbor in atomic layer orbitals will be second-neighbor in bond-orbitals.

It is equally true, of course, that a Hamiltonian which is only

nearest-neighbor in the bond-orbital representation may contain second-neighbor atomic parts.

The approximation comes about when all matrix elements are ignored except the $\langle b\ell' | H | b\ell \rangle$. In order to examine the feasibility of doing this, consider the sums

$$\begin{aligned} E_b(ka) &= \frac{1}{N} \sum_{\ell' \ell} \langle b\ell' | H | b\ell \rangle e^{ika(\ell - \ell')} \\ &= \frac{1}{2}(2g + \epsilon - 1 - \mu) + \frac{1}{2}(2\mu - 2 - \epsilon)\cos ka \\ &\quad - \frac{1}{2}(\mu + 1 + 2g)\cos 2ka. \end{aligned} \quad (168)$$

$$\begin{aligned} E_a(ka) &= \frac{1}{N} \sum_{\ell' \ell} \langle a\ell' | H | a\ell \rangle e^{ika(\ell - \ell')} \\ &= \frac{1}{2}(\epsilon + 1 + \mu - 2g) + \frac{1}{2}(2\mu - 2 + \epsilon)\cos ka \\ &\quad + \frac{1}{2}(\mu + 1 + 2g)\cos 2ka. \end{aligned} \quad (169)$$

and

$$\begin{aligned} V(ka) &= \frac{1}{N} \sum_{\ell' \ell} \langle b\ell' | H | a\ell \rangle e^{-ika(\ell' - \ell)} \\ &= \frac{1}{2}\epsilon i \sin ka + \frac{1}{2}(1 + \mu + 2g)i \sin 2ka. \end{aligned} \quad (170)$$

The bulk band structure would follow from the diagonalization of

$$H(ka) = \begin{pmatrix} E_b(ka) & V(ka) \\ V^*(ka) & E_a(ka) \end{pmatrix}. \quad (171)$$

The bonding-antibonding mixing is provided in (171) by V as defined in (170). This will be exactly zero if $\epsilon = 0$, $g = -\frac{\mu+1}{2}$. Thus, there exists an exact bond-orbital limit. In this limit, the eigenvalues of

$H(ka)$ become:

$$\omega_+(ka) = E_b = - (1+\mu) + (\mu-1)\cos ka \quad (172)$$

$$\omega_-(ka) = E_a = + (1+\mu) + (\mu-1)\cos ka,$$

which are exactly the expressions obtained from (111) for the valence and conduction band energies in the same limit. The exact validity of the bond-orbital model for the valence bands in this limit will be important when assessing the further application of this Hamiltonian to the computation of surface states.

Computation of the bulk Green function for the bond-orbital layers is exactly as in the one-band case above.

$$G_\ell^b = \frac{x_2 |\ell|}{(\mu-1) \sqrt{\left(\frac{\omega+1+\mu}{\mu-1}\right)^2 - 1}}, \quad (173)$$

$$x_2 = \left(\frac{\omega+1+\mu}{\mu-1}\right) - \sqrt{\left(\frac{\omega+1+\mu}{\mu-1}\right)^2 - 1}. \quad (174)$$

This Green function may be called the bond propagator.

Let

$$e = - (1+\mu), \quad m = \frac{1}{2}(\mu-1). \quad (175)$$

Then

$$G_\ell^b = \frac{x_2}{2m \sqrt{\left(\frac{\omega-e}{2m}\right)^2 - 1}} \quad (176)$$

Expression (176) now looks like (78).

2. Surface. In fact, (176) looks so much like (78) that it might be expected that the solution of the surface problem corresponding to (176) would lead to exactly the layer densities of states expressed by (87), with the replacements $\epsilon \rightarrow e$ and $\mu \rightarrow m$. It must be stressed that this is definitely not the case.

When a crystal is cleaved, bonds are broken. This results in a layer of dangling hybrid orbitals which do not arise naturally in a bond-orbital model when the crystal is terminated after the first bond-orbital layer. Actually, there would be a hybrid orbital pointing out into space beyond layer one. Bond orbital $|b,1\rangle$ contains parts of $|h^{(+)},1\rangle$ and $|h^{(-)},2\rangle$ but none of $|h^{(-)},1\rangle$, and so it is this dangling hybrid orbital which must be appended to the surface which allows the surface states to be computed within the otherwise bond-orbital model.

Imagine a basis set consisting of bond orbitals $1,2,3,\dots$ together with the dangling hybrid orbital. The bulk matrix elements of the Hamiltonian become

$$\langle b\ell' | H | b\ell \rangle = e\delta_{\ell',\ell} + m(\delta_{\ell',\ell+1} + \delta_{\ell',\ell-1}), \quad (177)$$

where e and m are related to the underlying two-band Hamiltonian in the bond-orbital limit by (175). However, in practice, the parameters of the bond-orbital Hamiltonian such as e and m in the simple example under consideration are determined by bulk properties, and the parameters of the unapproximated Hamiltonian remain unknown and are only

implicitly assumed to exist.

The diagonal matrix element which is the hybrid energy

$$\tau = \langle h^{(-)}, 1 | H | h^{(-)}, 1 \rangle \quad (178)$$

may be known from atomic measurements. Other matrix elements from bond-orbitals of the bulk to the surface hybrid must be evaluated using the decomposition of $h^{(-)}, 1$ in terms of bonding and antibonding parts.

$$\begin{aligned} \langle b, \ell | H | h^{(-)}, 0 \rangle = \\ \frac{1}{\sqrt{2}} \langle b, \ell | H | b, 0 \rangle - \frac{1}{\sqrt{2}} \langle b, \ell | H | a, 0 \rangle. \end{aligned} \quad (179)$$

However, the bonding-antibonding parts of these matrix elements will be unknown in a bond-orbital model. It is consistent to suppose that they are small, since this would have been the assumption in the bulk calculation. In fact, there is no other choice. If they are not set to zero, more parameters are introduced at this late stage of the calculation. This seriously erodes any legitimacy which this approach may have had up until this point. In the present example calculation, there is no difficulty with this assumption since the bond-orbital limit which has been taken forces all bonding-antibonding matrix elements to be exactly zero. Thus

$$\langle b, 1 | H | h^{(-)}, 1 \rangle = \frac{1}{\sqrt{2}} m, \quad (180)$$

while all others are zero.

The computation now proceeds as follows. If the hybrid orbital

layer were not connected to the bulk by the matrix element of (180), then the propagator for the stage on the disconnected hybrid would be simply

$$J_{00} = (\omega - \tau)^{-1} \quad (181)$$

while the Green function on the surface of the bond-orbital substrate would be given from the results of the one-band problem by

$$J_{11} = \frac{1}{m} \left[\left(\frac{\omega - e}{2m} \right) - \sqrt{\left(\frac{\omega - e}{2m} \right)^2 - 1} \right]. \quad (182)$$

Using the expression (51) which relates the final propagator to these uncoupled Green functions, the resolvent on the dangling hybrid becomes

$$R_{00} = (\omega - \tau - \frac{1}{2} m^2 J_{11})^{-1} \quad (183)$$

The poles in ω of this function signals the occurrence of a bound surface state. The approximate gap state energy thus becomes

$$\omega = \frac{1}{2}(1+\mu) - \frac{1}{2}\sqrt{(1+\mu)^2 - \frac{1}{2}(1-\mu)^2}. \quad (184)$$

The trajectory of this state is plotted in figure 9 as a function of μ , together with the positions of the band edges. The actual gap state energy in the two-band model was $\epsilon/(1+\mu)$, but in this bond-orbital limit, $\epsilon = 0$, so the gap state should appear at zero energy. In figure 9, the actual gap state is labeled A and the bond-orbital approximation to it is labeled B. The conduction band minimum is linear as a function of μ and is represented by a dashed line. The

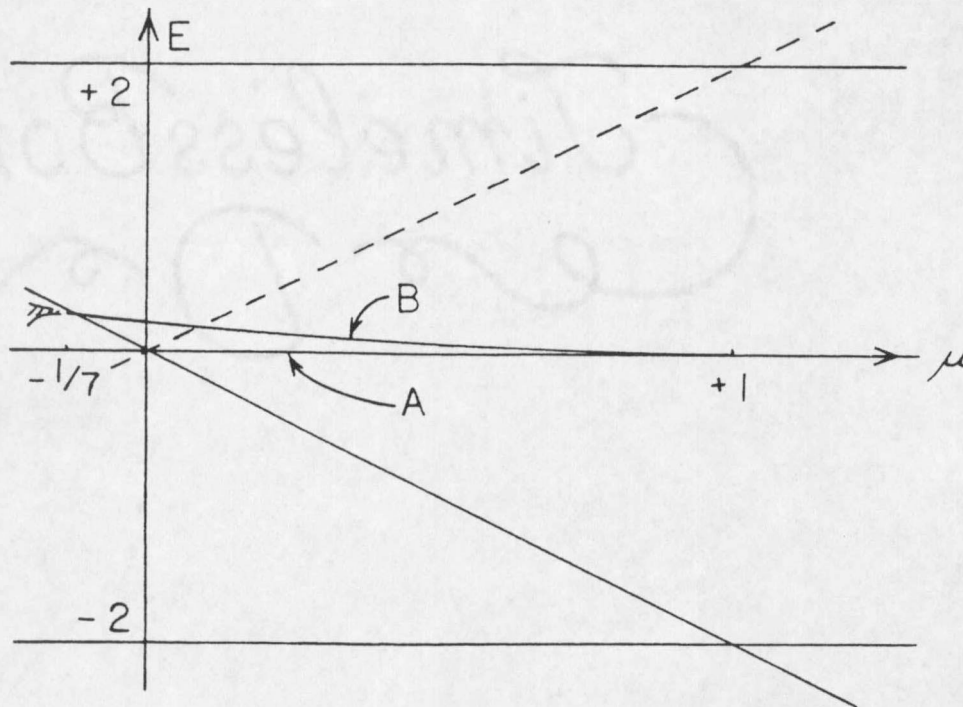


Figure 9. Bond-Orbital Approximation to the Gap State Energy in the Two Band Model. The parameter determines the band gap. The valence band extends between 2 and the slanted, solid line while the conduction band extends between the slanted, dashed line and +2. Energy is in quarter s-band units. A is the energy of the actual gap state, while the bond-orbital approximation gives B.

valence band maximum is also linear and is represented by a solid line with equal but opposite slope. For any given value of μ the valence band extends from -2 up to -2μ , while the conduction band is between 2μ and 2 .

As the bands become narrow compared to the gap, the bond-orbital approximation is to remove the conduction bands. Coupling to the conduction bands would repel the surface state downward by an amount equal and opposite to that of the valence bands. In other words, although the valence and conduction bands do not interact in the bond-orbital limit, each interacts separately with the surface hybrid. The approximation which is being made is to neglect the coupling between the hybrid and the conduction band. Thus the upward push from the valence band is not balanced by the downward push which would have been exerted by the conduction bands.

There are two reasons why the bond-orbital approach may yet be justified in the study of semiconductor surface states. First, the graph of figure 9 shows that if the gap is not extremely narrow compared to the band width, the approximation may not be so bad. Second, in more realistic bond-orbital models used for semiconductor valence bands, the energy of the filled hybrid gap state is much closer to the valence band maximum, and so the influence of the conduction bands might reasonably be expected to be much smaller.

The purpose of this section has been to point out the

approximations involved in a bond-orbital model and to warn the reader of the possible shortcomings of these approximations when the model is applied to the solution of the surface problem.

IV. BOND-ORBITAL MODEL OF HARRISON

A. Bulk Chemistry

1. Formation of bond-orbitals. In this section a bond-orbital model will be presented which was developed by Harrison, Pantelides and Ciraci^{31,35,36} and has been used by them to investigate bulk and surface^{32-34,37} properties of zincblende-type semiconductors.

Start with an s and three p atomic states on each cation site and the same on each anion site. For the moment, it is not important to consider the details of the geometry. Consider two sp^3 hybrids, one on an anion pointing toward a neighboring cation and one the cation pointing back toward the first as illustrated in figure 10. $|h_a\rangle$ is the orbital on the anion and $|h_c\rangle$ is the orbital on the cation. The overlap

$$S = \langle h_a | h_c \rangle \quad (189)$$

between two such hybrids which extend directly toward one another has been reported to be large³⁸ and cannot be neglected. Define two parameters in terms of which the bond formation may be discussed:

ionicity

$$M_3 = \frac{1}{2}(\epsilon^C - \epsilon^A) \quad (190)$$

covalency

$$M_2 = -\langle h_a | H | h_c \rangle. \quad (191)$$

Selecting as the zero of energy the mean energy of the hybrids

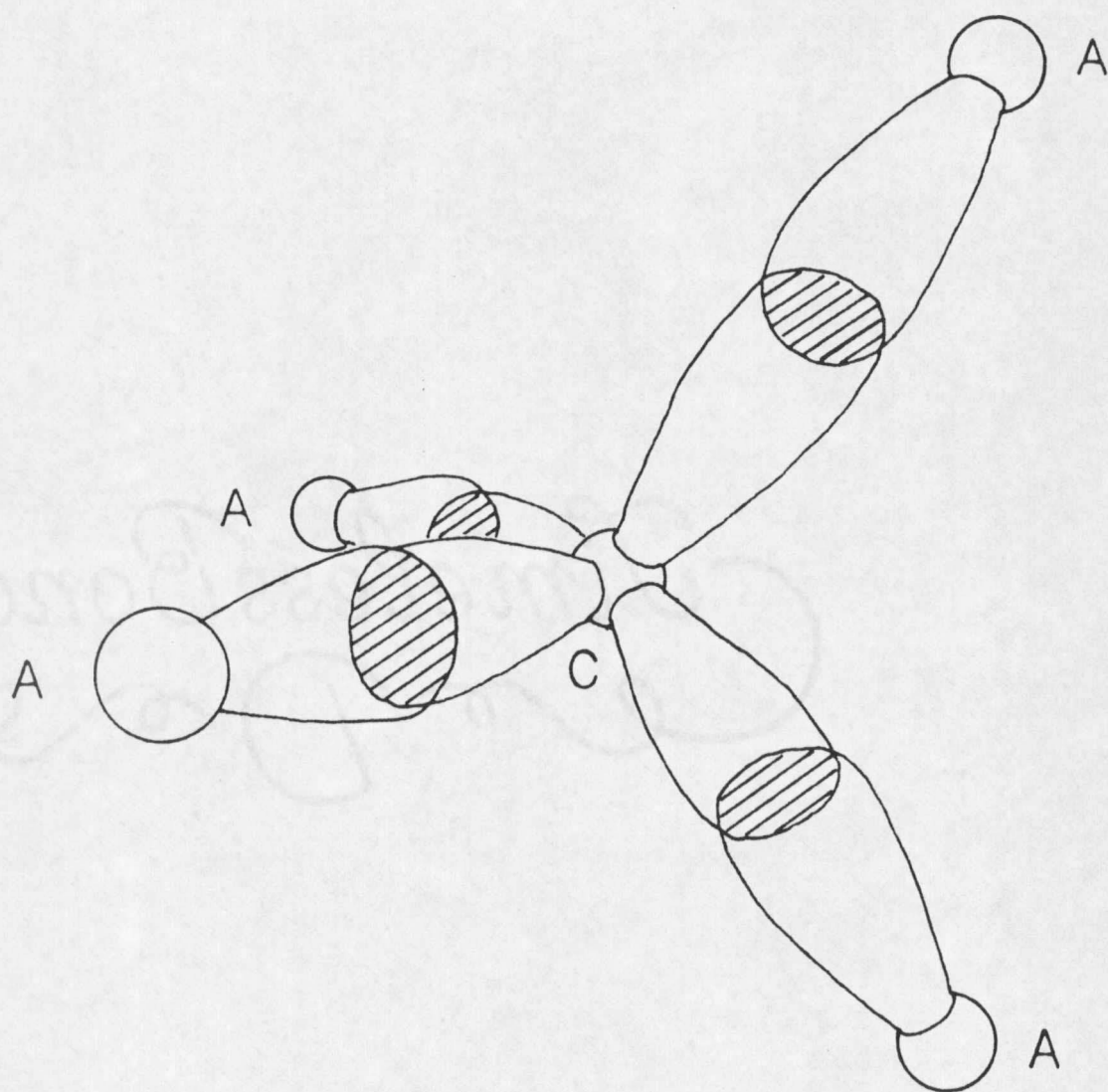


Figure 10. sp^3 Hybrid Orbitals on a Cation C Pointing Toward Neighboring Anions A.

$$\text{energy zero} = \frac{1}{2}(\epsilon^c + \epsilon^a) \quad (192)$$

the bond formation becomes, as it did in the previous section, a 2 times 2 eigenvalue problem. This time, however, non-orthogonality of the orbitals must be carefully handled. The 2 times 2 Hamiltonian is

$$H = \begin{pmatrix} -M_3 & -M_2 \\ -M_2 & M_3 \end{pmatrix} \quad (193)$$

while the overlap matrix

$$\Sigma = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \quad (194)$$

The first row (column) corresponds to the anion in each case. One must solve

$$(H - E\Sigma)|\psi\rangle = 0 \quad (195)$$

in order to get the mixing coefficients which determine the bond-orbitals. Next, transform the components of $|\psi\rangle$.

$$|\psi\rangle = \Sigma^{-\frac{1}{2}}|\phi\rangle. \quad (196)$$

Then

$$(\Sigma^{-\frac{1}{2}}H\Sigma^{-\frac{1}{2}} - E)|\phi\rangle = 0. \quad (197)$$

Note that since H and Σ are Hermitian, so is $\Sigma^{-\frac{1}{2}}H\Sigma^{-\frac{1}{2}}$. Rather than transform the components of the orbital, as in (196), it is equivalent to transform the basis vectors $|h_a\rangle$ and $|h_c\rangle$. To do this, $\Sigma^{-\frac{1}{2}}$ is needed.

The eigenvectors of Σ corresponding to its eigenvalues $(1+s)$ and

(1-s) are

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \text{ and } \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \quad (198)$$

Thus

$$\Sigma = (1+s) \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} + (1-s) \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \quad (199)$$

And so

$$\Sigma^{-\frac{1}{2}} = \frac{1}{2\sqrt{1-s^2}} \begin{pmatrix} \sqrt{-} + \sqrt{+} & \sqrt{-} - \sqrt{+} \\ \sqrt{-} - \sqrt{+} & \sqrt{-} + \sqrt{+} \end{pmatrix}, \quad (201)$$

where

$$\sqrt{+} = \sqrt{1+s}, \text{ and } \sqrt{-} = \sqrt{1-s}.$$

Thus the new, orthogonalized basis set becomes:

$$|h_a^*\rangle = \frac{1}{2\sqrt{1-s^2}} [(\sqrt{-} + \sqrt{+})|h_a\rangle + (\sqrt{-} - \sqrt{+})|h_c\rangle], \quad (202)$$

$$|h_c^*\rangle = \frac{1}{2\sqrt{1-s^2}} [(\sqrt{-} - \sqrt{+})|h_a\rangle + (\sqrt{-} + \sqrt{+})|h_c\rangle].$$

The basis of (202) may be easily seen to be orthonormal using (189).

The H matrix of (193) may now be expressed in terms of $|h_a^*\rangle$ and $|h_c^*\rangle$ as an H^* matrix.

$$H^* = \begin{pmatrix} -V_3 + SV_2 & V_2 \\ -V_2 & V_3 + SV_2 \end{pmatrix} \quad (203)$$

where

$$V_2 = \frac{M_2}{(1-s^2)} \quad (204)$$

$$V_3 = \frac{M_3}{\sqrt{1-s^2}} \quad (205)$$

The energy eigenvalues of this matrix are the extreme values of the bond energy. The eigenvector corresponding to the minimum bond energy gives the mixture coefficients for the bond-orbital while the eigenvector of the largest eigenvalue gives the antibond mixture coefficients. The bond and antibond energies are respectively

$$E_b = SV_2 - \sqrt{V_2^2 + V_3^2} \quad (206)$$

$$E_a = SV_2 + \sqrt{V_2^2 + V_3^2} \quad (207)$$

where the energy zero (192) must be added in order to find the absolute energies.

In their bulk calculation, Pantelides and Harrison³⁵, whose parameters will be used in the computation below, have not concerned themselves with the overlap S . These orthogonality corrections enter explicitly at the surface layer where non-orthogonalized hybrids form the dangling hybrid surface states. Thus the transformation between the bond-orbitals of the bulk basis set and the original hybrid orbitals must be worked out in detail. Strange as it may seem, the

expansion coefficients for the antibond-orbitals will also be needed so that, as was done in the simpler example above, the hybrids may be expanded in terms of bonding and antibonding parts. Let $|b\rangle$ be a bond orbital and $|a\rangle$ be an antibond-orbital.

$$|b\rangle = u_a |h_a\rangle + u_c |h_c\rangle, \quad (208)$$

where

$$u_a = \frac{1}{2\sqrt{2}(1-S^2)} [(\sqrt{+}\sqrt{-})\sqrt{1+\alpha_p} - (\sqrt{+}\sqrt{-})\sqrt{1-\alpha_p}] \quad (209)$$

$$u_c = \frac{1}{2\sqrt{2}(1-S^2)} [(\sqrt{+}\sqrt{-})\sqrt{1-\alpha_p} - (\sqrt{+}\sqrt{-})\sqrt{1+\alpha_p}], \quad (210)$$

and likewise

$$|a\rangle = v_a |h_a\rangle + v_c |h_c\rangle \quad (211)$$

with

$$v_a = \frac{1}{2\sqrt{2}(1-S^2)} [(\sqrt{+}\sqrt{-})\sqrt{1-\alpha_p} + (\sqrt{+}\sqrt{-})\sqrt{1+\alpha_p}], \quad (212)$$

$$v_c = \frac{1}{2\sqrt{2}(1-S^2)} [(\sqrt{+}\sqrt{-})\sqrt{1+\alpha_p} + (\sqrt{+}\sqrt{-})\sqrt{1-\alpha_p}]. \quad (213)$$

The symbol α_p used in (209-213) is defined by

$$\alpha_p = V_3(V_2^2 + V_3^2)^{-1/2}. \quad (214)$$

It is related to the charge transfer per electron in the bond-orbital by

$$|u_a|^2 - |u_c|^2 = \alpha_p / \sqrt{1-S^2} \quad (215)$$

For this reason, α_p is called^{31,36} the bond polarity, since it reduces to that as S goes to zero.

Before leaving the subject of bond formation and the basis set and moving on to the definition of bulk matrix elements, one last operation must be performed. The transformation equations (208-213) must be inverted in order to obtain $|h_a\rangle$ and $|h_c\rangle$ as functions of $|b\rangle$ and $|a\rangle$. This is the form in which the connection will be needed when the surface perturbation is defined.

$$|h_a\rangle = C_1|b\rangle + C_3|a\rangle \quad (216)$$

$$|h_c\rangle = C_2|b\rangle + C_4|a\rangle \quad (217)$$

with

$$C_1 = v_c/\Delta, C_3 = -u_c/\Delta, \quad (218)$$

$$C_2 = v_a/\Delta, C_4 = u_a/\Delta,$$

where $\Delta = u_a v_c - u_c v_a$ is the determinant of the transformation. Quite simply,

$$\Delta = -1/\sqrt{1-S^2}. \quad (219)$$

Thus the coefficients C_1 and C_2 , which will be needed later are

$$C_1 = \frac{1}{2\sqrt{2}} [(\sqrt{+}\sqrt{-})\sqrt{1-\alpha_p} + (\sqrt{++}\sqrt{-})\sqrt{1+\alpha_p}] \quad (220)$$

$$C_2 = \frac{1}{2\sqrt{2}} [(\sqrt{++}\sqrt{-})\sqrt{1-\alpha_p} + (\sqrt{+-}\sqrt{-})\sqrt{1+\alpha_p}] \quad (221)$$

2. Bond-orbital matrix elements. Each ion in a semi-conductor of the zincblende structure is tetrahedrally coordinated. The four bond-orbitals surrounding a cation, for example, are each formed from a linear combination of hybrid orbitals, one on the cation and one on a neighboring anion. Figure 10 illustrates a tetrahedral arrangement of hybrid orbitals which, in figure 11, have been used to form bond-orbitals in the manner described above.

Because the (110) surface of zincblende semiconductors will be treated below, it is expedient to define a coordinate set as follows³⁹. The z-direction will be perpendicular to the (110) surface pointing out of the crystal; the x-direction will be perpendicular to the (100) plane, and the y-direction forms a right-handed coordinate system.

The basis set for the bulk of the crystal consists of four, inequivalent bond-orbitals. Figure 11 shows the basis set arranged in a tetrahedron about the cation position. With respect to the newly-defined coordinate system, the directions of the bulk basis states are

$$|b1\rangle \rightarrow (1/3, 0, 2\sqrt{2}/3) \quad (222)$$

$$|b2\rangle \rightarrow (1/3, 0, -2\sqrt{2}/3)$$

$$|b3\rangle \rightarrow (-1/3, 2\sqrt{2}/3, 0)$$

$$|b4\rangle \rightarrow (-1/3, -2\sqrt{2}/3, 0).$$

The orbitals defined in (222) are arranged on an fcc lattice and form the zincblende structure, as illustrated in figure 12. Notice that the use of bond-orbitals focuses attention on the bonds rather

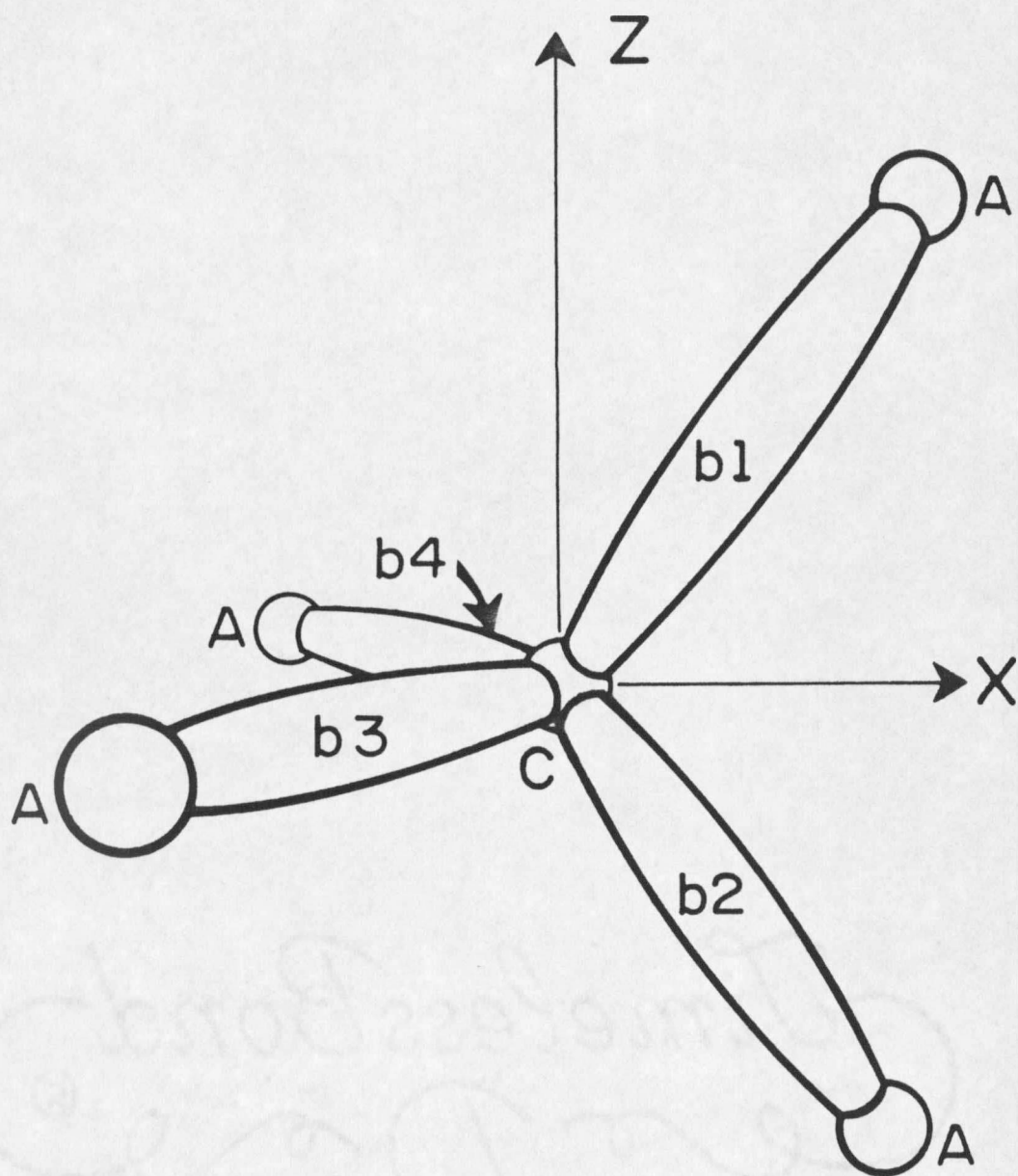


Figure 11. Tetrahedron of Bond-Orbitals.

The y-axis is pointing out of the paper.

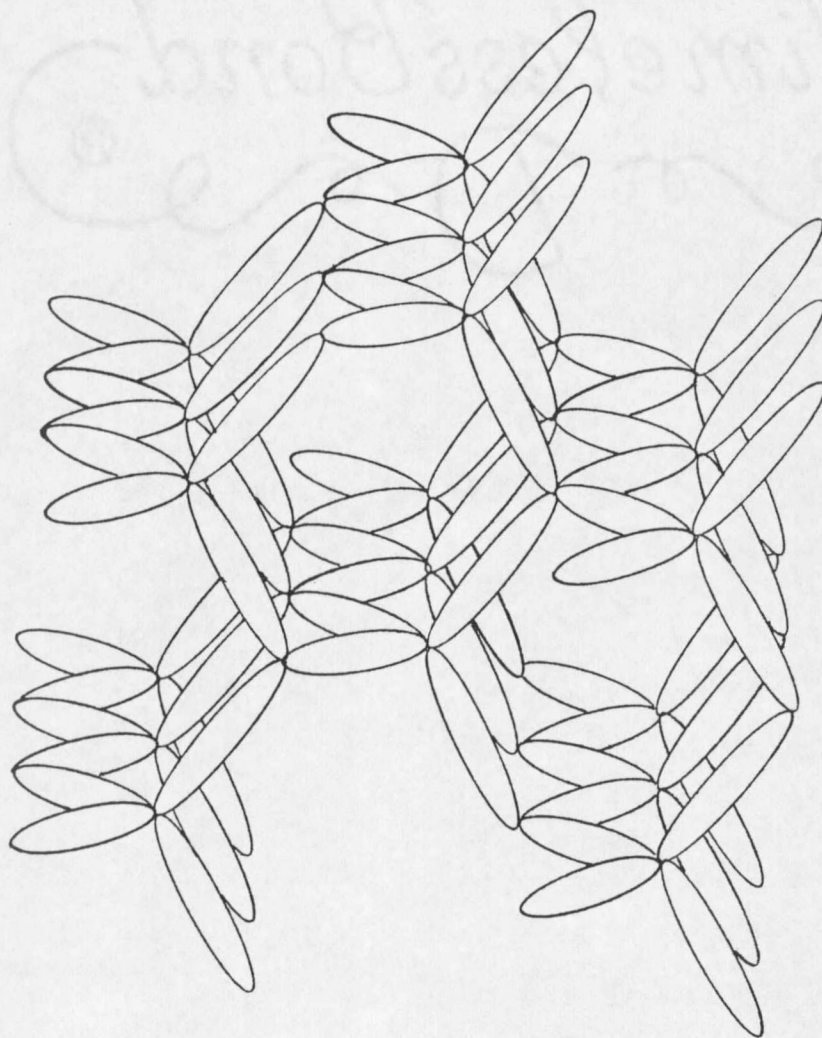


Figure 12. The Zincblende Structure is Formed by Stacking the Cation Jacks of Bond-Orbitals as Shown in figure 11 into an fcc Lattice.

Notice how well this basis set corresponds with the intuitive, ball-and-stick notion of the crystal bonding.

than the atoms themselves; thus the valence bands become associated with a framework model of the crystal. The crystal model is, in fact, a graphical representation of the bond-orbital Hamiltonian.

Pantelides and Harrison³⁵ have shown that except in the case of compounds containing the carbon row elements, the bulk properties of zincblende-type semiconductors are well reproduced using only three matrix element parameters. These are presented in figure 13. B_1^C and B_1^A are minus the nearest-neighbor matrix elements between bonds which have a common vertex at either a cation site or an anion site respectively. B_4 is minus the matrix element between second-neighbor bonds which are parallel. Another matrix element would be needed in order to treat those compounds which contain a carbon row element. Such compounds will not be treated in the present work. For convenience, the parameters

$$\begin{aligned} B_1^S &= \frac{1}{2}(B_1^A + B_1^C) \\ B_1^a &= \frac{1}{2}(B_1^A - B_1^C) \end{aligned} \tag{223}$$

are introduced.

In all then, three parameters suffice to determine the bulk band structure, namely B_1^S , B_1^a , and B_4 .

B. Surface Definition

1. Surface matrix elements. Four coupling coefficients are required in order to describe the way in which the dangling hybrids connect to

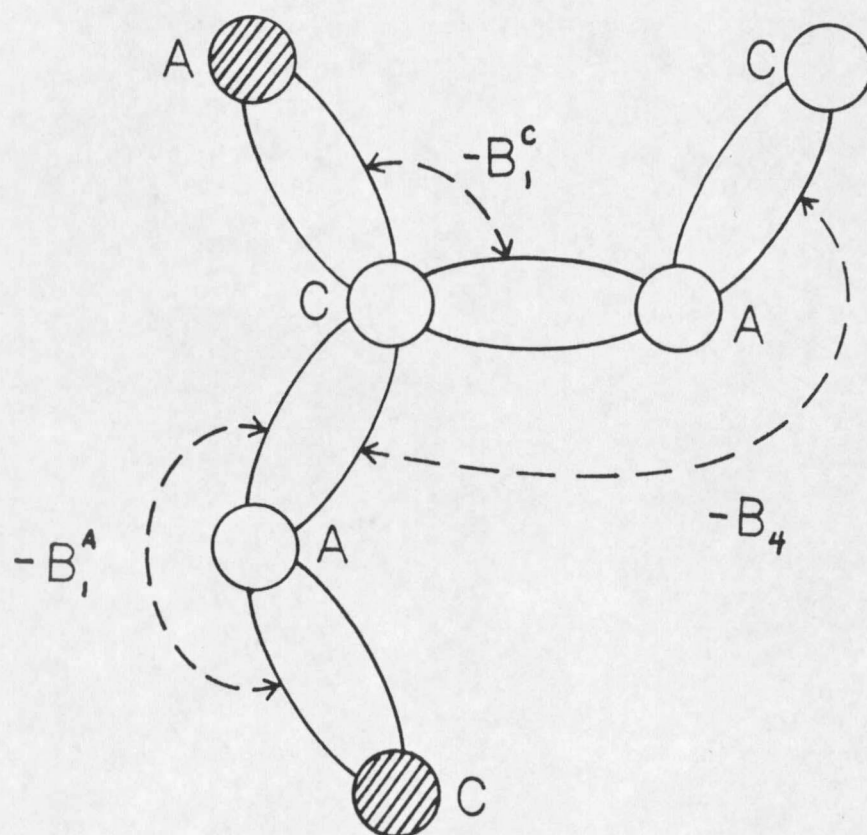


Figure 13. The Bond-Orbital Matrix Elements of Pantelides and Harrison. Open circles represent ions on a given (110) plane, while the cross-hatched circles represent ions in a lower plane.

the bulk. These are presented in figure 14.

For example, consider g_1 .

$$g_1 = \langle b_4 | H | h_c \rangle. \quad (224)$$

Using (217),

$$g_1 = C_2 \langle b_4 | H | b_1 \rangle + C_4 \langle b_4 | H | a_1 \rangle \quad (225)$$

As in the two-band model, the bonding-antibonding part must be dropped.

$$g_1 = C_2 (-B_1^C) \quad (226)$$

$$= \frac{-1}{2\sqrt{2}} [(\sqrt{+} + \sqrt{-}) \sqrt{1-\alpha_p} + (\sqrt{+} - \sqrt{-}) \sqrt{1+\alpha_p}] B_1^C.$$

Likewise,

$$g_2 = C_2 (-B_4) \quad (227)$$

$$= \frac{-1}{2\sqrt{2}} [(\sqrt{+} + \sqrt{-}) \sqrt{1-\alpha_p} + (\sqrt{+} - \sqrt{-}) \sqrt{1+\alpha_p}] B_4,$$

$$g_3 = C_1 (-B_1^A) \quad (228)$$

$$= \frac{-1}{2\sqrt{2}} [(\sqrt{+} - \sqrt{-}) \sqrt{1-\alpha_p} + (\sqrt{+} + \sqrt{-}) \sqrt{1+\alpha_p}] B_1^A,$$

$$g_4 = C_1 (-B_4) \quad (229)$$

$$= \frac{-1}{2\sqrt{2}} [(\sqrt{+} - \sqrt{-}) \sqrt{1-\alpha_p} + (\sqrt{+} + \sqrt{-}) \sqrt{1+\alpha_p}] B_4.$$

2. Bravais lattice. A set of translation vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$ is illustrated in figure 15. These generate the Bravais lattice, which is fcc. A tetragonal unit cell which is useful in computations, although

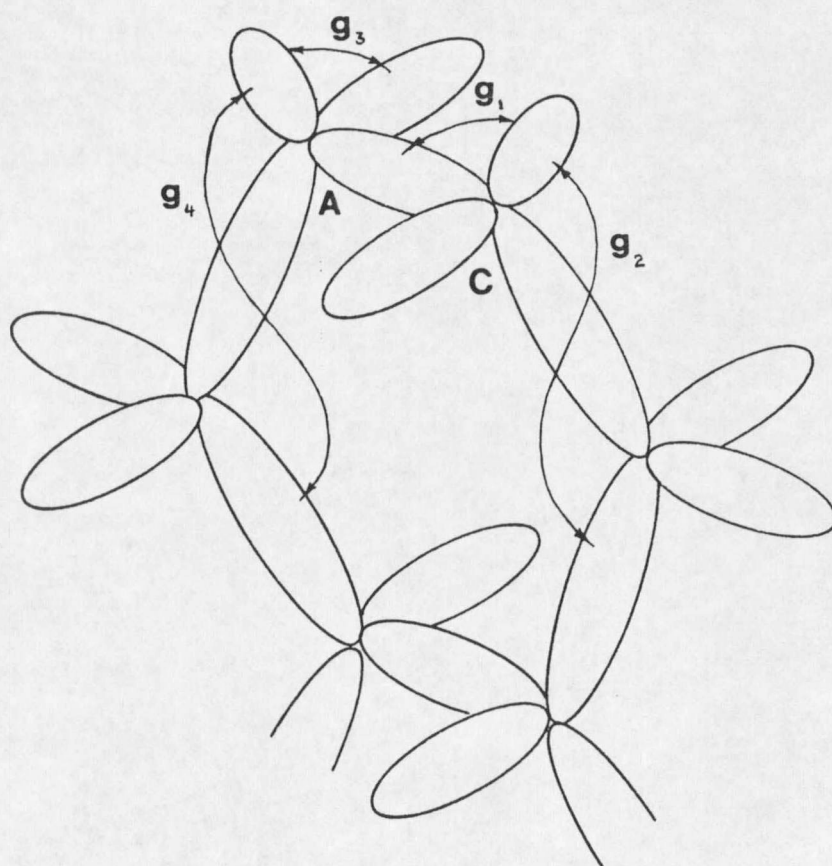


Figure 14. Matrix Elements Which Couple the Dangling Hybrids Back into the Bulk.

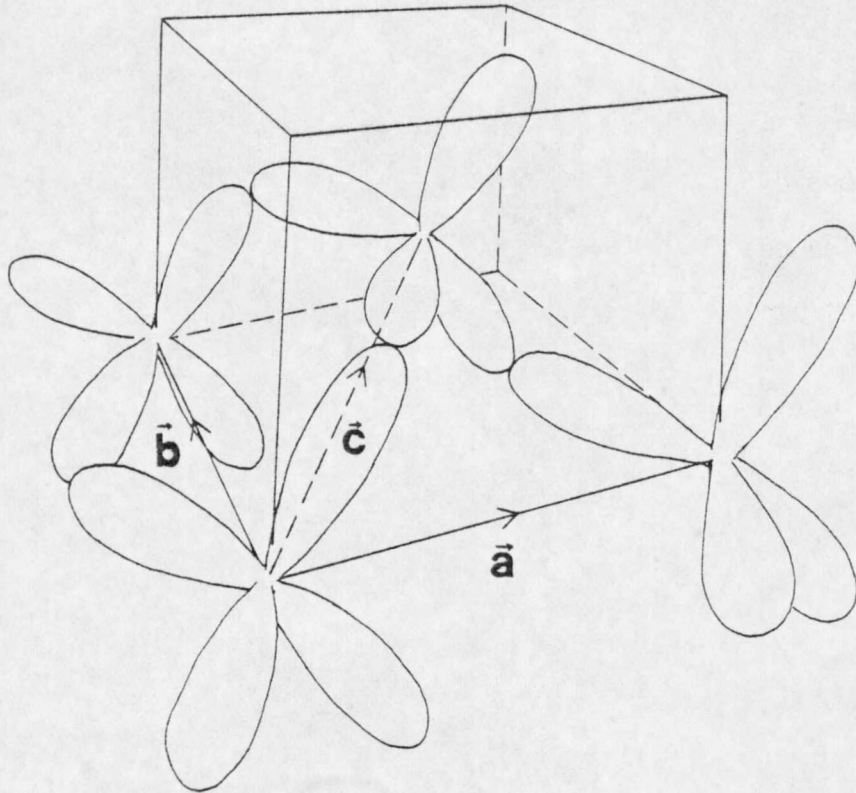


Figure 15. Non-Primitive, Tetragonal Unit Cell Used in Order to Demonstrate the Basis Vectors $\vec{a}$, $\vec{b}$ and $\vec{c}$. $\vec{c}$ extends from the corner to the center of the cell. $\vec{a}$ forms one edge of the square base and $\vec{b}$ forms the long edge.

it is not primitive, is also illustrated. The components of the translation vectors in terms of the coordinate directions defined above are

$$\vec{a} = a \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \vec{b} = \frac{1}{\sqrt{2}} a \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \vec{c} = \frac{1}{2\sqrt{2}} a \begin{pmatrix} \sqrt{2} \\ 1 \\ 1 \end{pmatrix}. \quad (230)$$

The symbol a in (230) stands for the length of the edge of the conventional (cubic) unit cell. The positions of the cation sites are then defined in terms of these by

$$\vec{r}_{\ell, m, n} = \ell \vec{a} + m \vec{b} + n \vec{c} \quad (231)$$

where ℓ , m and n are integers. The bond-orbitals distributed about a cation at site ℓ , m , n are denoted by

$$|\mu, \ell, m, n\rangle \quad (232)$$

μ denoting which bond-orbital, as in (222) and ℓ , m and n prescribing the position of the cation vertex. Bulk matrix elements of the Hamiltonian between states so defined are presented in Appendix A.

3. Layer-orbitals. Notice in (232) that a change in the indices ℓ and m is associated with a change from one orbital to an equivalent orbital in the same (110) layer, while a change in n implies a change in layer.

As in the simpler examples, suppose for the moment that N_1 by N_2 states of a given type are on each layer. With periodic boundary conditions in the plane of the layer, layer-orbitals may be defined by

$$|v, k_1, k_2, n\rangle = \frac{1}{\sqrt{N_1 N_2}} \sum_{\ell m} e^{i \vec{k}_{||} \cdot \vec{r}_{\ell mn}} |v, \ell, m, n\rangle \quad (233)$$

The components k_1, k_2 of $\vec{k}_{||}$ are the cartesian components parallel to the surface

$$\vec{k}_{||} = k_1 \hat{x} + k_2 \hat{y}. \quad (234)$$

Thus the exponent in (233) is

$$\vec{k}_{||} \cdot \vec{r}_{\ell mn} = \ell k_1 a + \frac{m k_2 a}{\sqrt{2}} + \frac{n}{2} \left(k_1 a + \frac{k_2 a}{\sqrt{2}} \right). \quad (235)$$

Again, in terms of these layer-orbitals, matrix elements of the bulk Hamiltonian may be computed. Because of momentum conservation, only matrix elements between states of the same $\vec{k}_{||}$ will be non-zero. This was, as will be recalled, the motivation for the transformation to layer orbitals. The diagonal (in $\vec{k}_{||}$) elements of H are

$$H_{n'n}^{\mu\nu}(\vec{k}_{||}) = (s_1 s_2)^{(n-n')} \sum_{\ell m} s_1^{-2\ell} s_2^{-2m} \langle \mu \ell mn' | H | \nu 0 0 n \rangle, \quad (236)$$

where the structure factors

$$s_1 = e^{ik_1 a/2}, \quad s_2 = e^{ik_2 a/2\sqrt{2}}$$

These matrix elements are computed using Appendix A and tabulated in Appendix B.

V. MATRIX SLAB CALCULATION

A. Implementation

1. Bulk. The procedure of finding the eigenvalues and eigenvectors of a thin film of GaAs with (110) surfaces is essentially one of diagonalization of a large matrix which has one row (or column) for each orbital at a given $\vec{k}_{||}$. This problem is logically divisible into two parts: defining the matrix elements and performing the diagonalization. The diagonalization is done numerically⁴⁰ and the bulk part of the matrix has elements as defined in Appendix B.

Arranging the layer-orbitals for a particular value of $\vec{k}_{||}$ into numerical order may be done according to

$$|m\rangle = |\mu, k_1, k_2, n\rangle \quad (238)$$

where

$$m = 4(n-1) + \mu$$

Thus, if there were 8 layers in the slab, then the basis set would contain 32 states. The notation of (238) will be used until the end of the present chapter. Appendix B would now provide the matrix elements of the layer-orbital bulk Hamiltonian.

2. Surface. Simply terminating the bulk Hamiltonian at layer $n=0$ and layer $n=N$ creates a surface of the type investigated by Shockley in 1939³⁰. As has been discussed in the two-band case, this Shockley surface is unrealistic for a bond-orbital bulk Hamiltonian.

Consider a Shockley surface formed in such a way as to remove all bond-orbitals beyond a given layer, say for definiteness layer 1, as shown in figure 16. Then the bond-orbitals of state $|1\rangle$ would stick out of the surface at the cation sites while no states at all would protrude from the anion states.

Two important changes must be made in order to correctly represent a realistic surface as presented in figure 17. First the dangling bond-orbital on each surface cation site, both at layer 1 and at layer N, must be replaced by a cation hybrid orbital. This means that each matrix element involving either $|1\rangle$ or $|4N-2\rangle$ must be replaced in the slab Hamiltonian. Second, states must be added to the basis set which represent the anion dangling hybrids. Matrix elements involving the added states must be added to the Hamiltonian. These added states have been called $|0\rangle$ and $|4N+1\rangle$. Surface coupling matrix elements needed to effect these changes are presented in Appendix C.

Expressions (230) for the lattice translation vectors induce a surface Brillouin zone as depicted in figure 18. The edges of the zone are at $k_1 = \pm \frac{\pi}{a}$ and $k_2 = \pm \frac{\sqrt{2}\pi}{a}$. Symmetry points and lines of the surface zone are labeled in the notation of Jones⁴¹.

B. Results and Discussion

We have used the bond-orbital model of Pantelides and Harrison to compute eigenvalues and eigenstates of a twelve-layer slab according to the method described in detail above. Dispersion plots of the

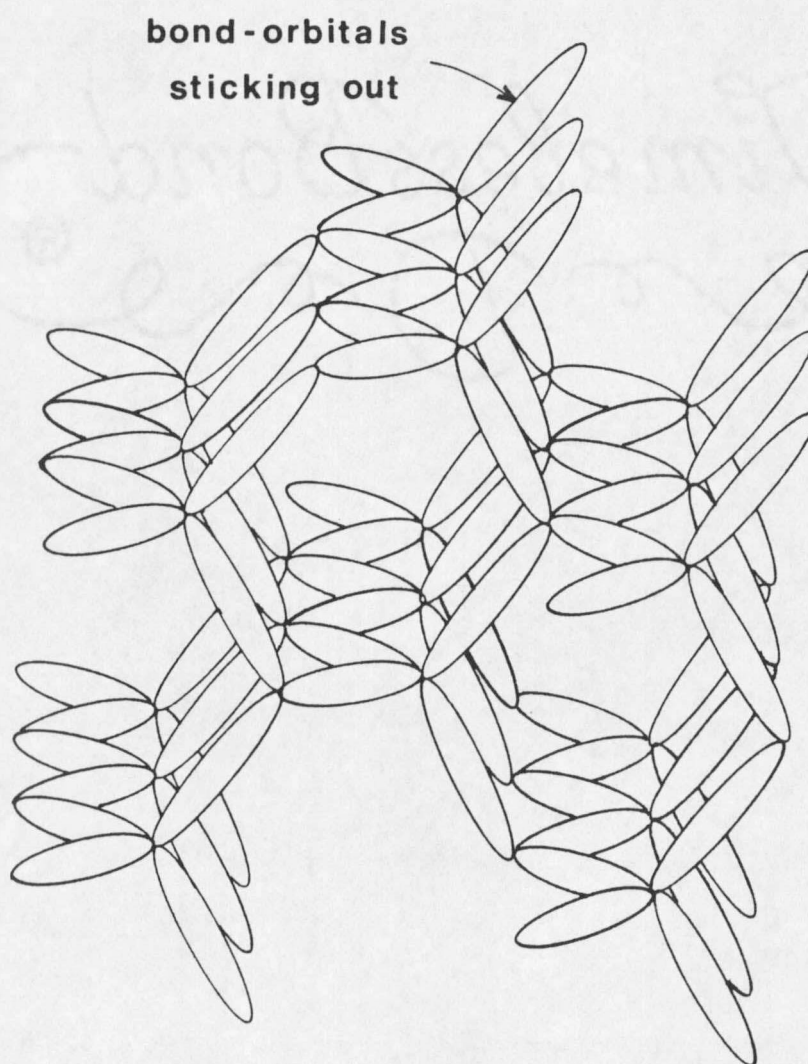


Figure 16. Result of Truncating the Bulk Hamiltonian.

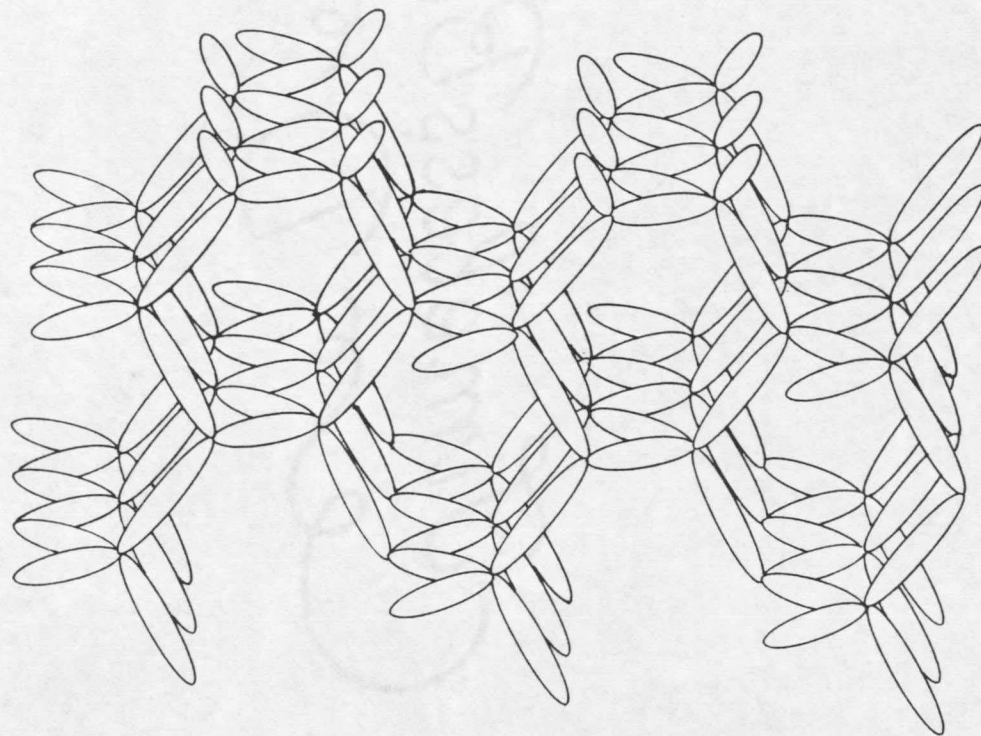


Figure 17. More Realistic Surface with Dangling Hybrid Orbitals.

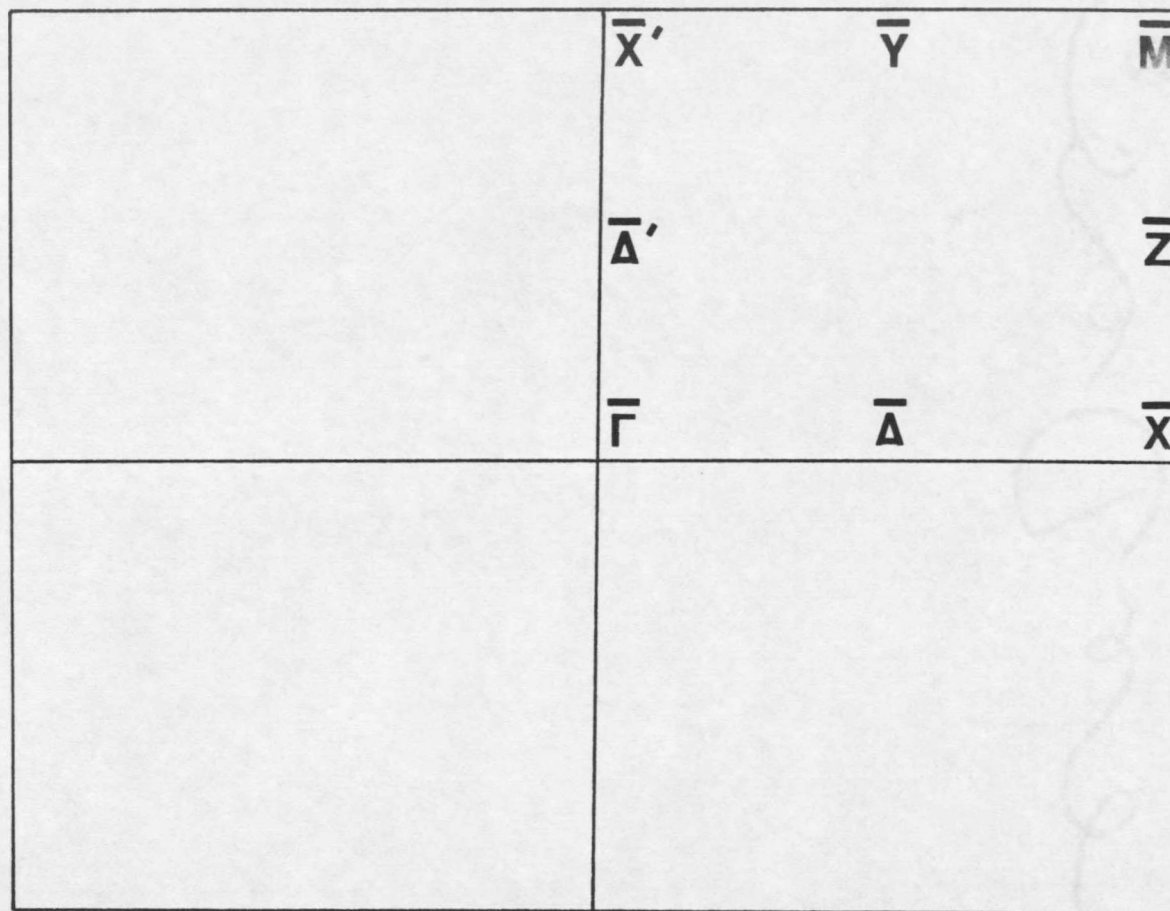


Figure 18. Surface Brillouin Zone.

$\bar{\Delta}'$ is along x-axis while $\bar{\Delta}$ is along y.

surface states appear in figure 19 together with the projected bulk bands.

The labels B_1 , B_2 and B_3 used to denote the surface states are those introduced by Joannopoulos and Cohen³ who have computed eigenstates for a twelve-layer slab using an eight state basis set of hybrid-orbitals. Considering the simplicity of the present model, the results agree rather well with those of Joannopoulos and Cohen. There are two states in the optical gap: B'_1 (which is not shown) is the cation dangling bond state and B_1 is due to the dangling anion hybrids. There is also a state B_3 in the heteropolar gap near the lower valence bands, and a state B_2 which lies near the bottom of the gap that opens in the upper valence bands away from the center of the surface Brillouin zone.

Figure 20 shows the probability distribution for an electron in the B_1 surface state at the $\bar{\Gamma}$ point, which corresponds to normal photoemission. An electron in this state spends 62% of its time on the anion dangling bond, 10% on the cation back bond and a total of 10% on the two parallel bonds which run along the surface. The total localization on the surface layer is about 82%. If the same state is examined at the $\bar{M}$ point, the electron density is 82% on the anion dangling bond and 9% in the parallel bonds. Another 5% is in the anion back bond, making a total localization of 96%. This increased localization is due to the fact that the B_1 state is separated far from the bulk

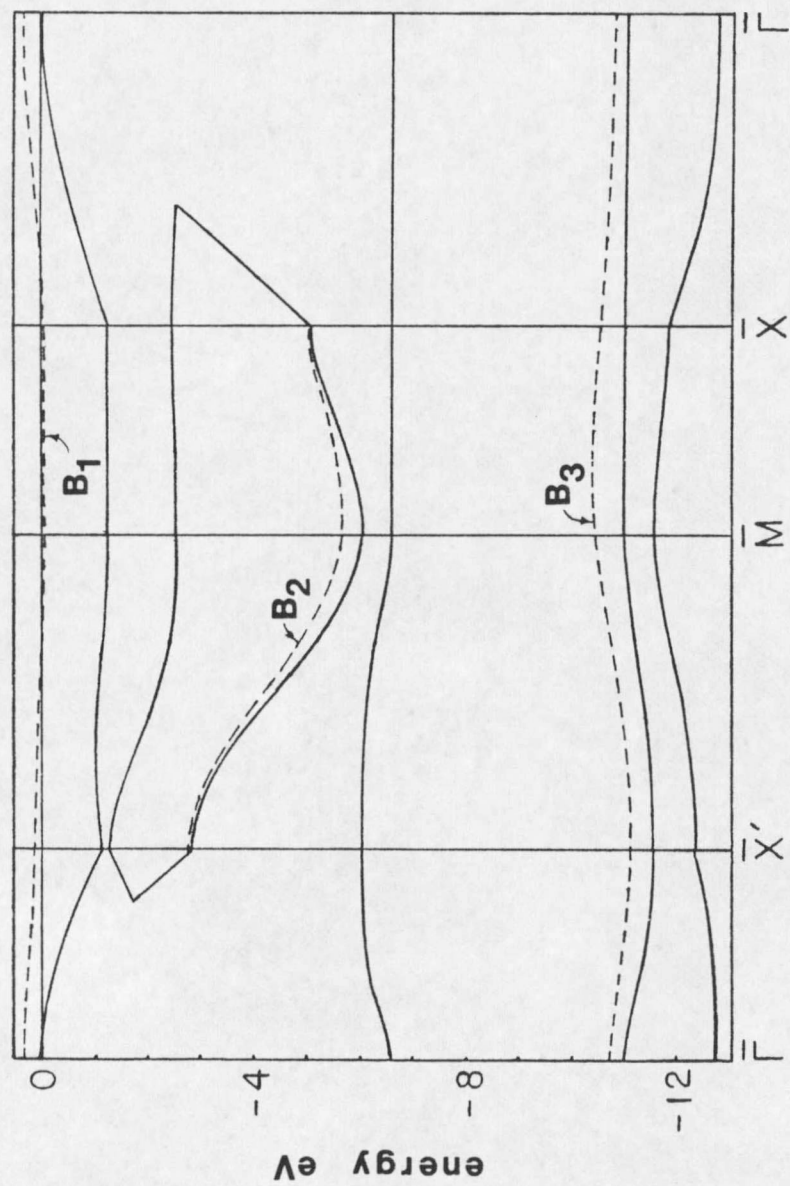


Figure 19. Surface States on the Unrelaxed (110) Surface of GaAs. Zero of energy is the valance band maximum.

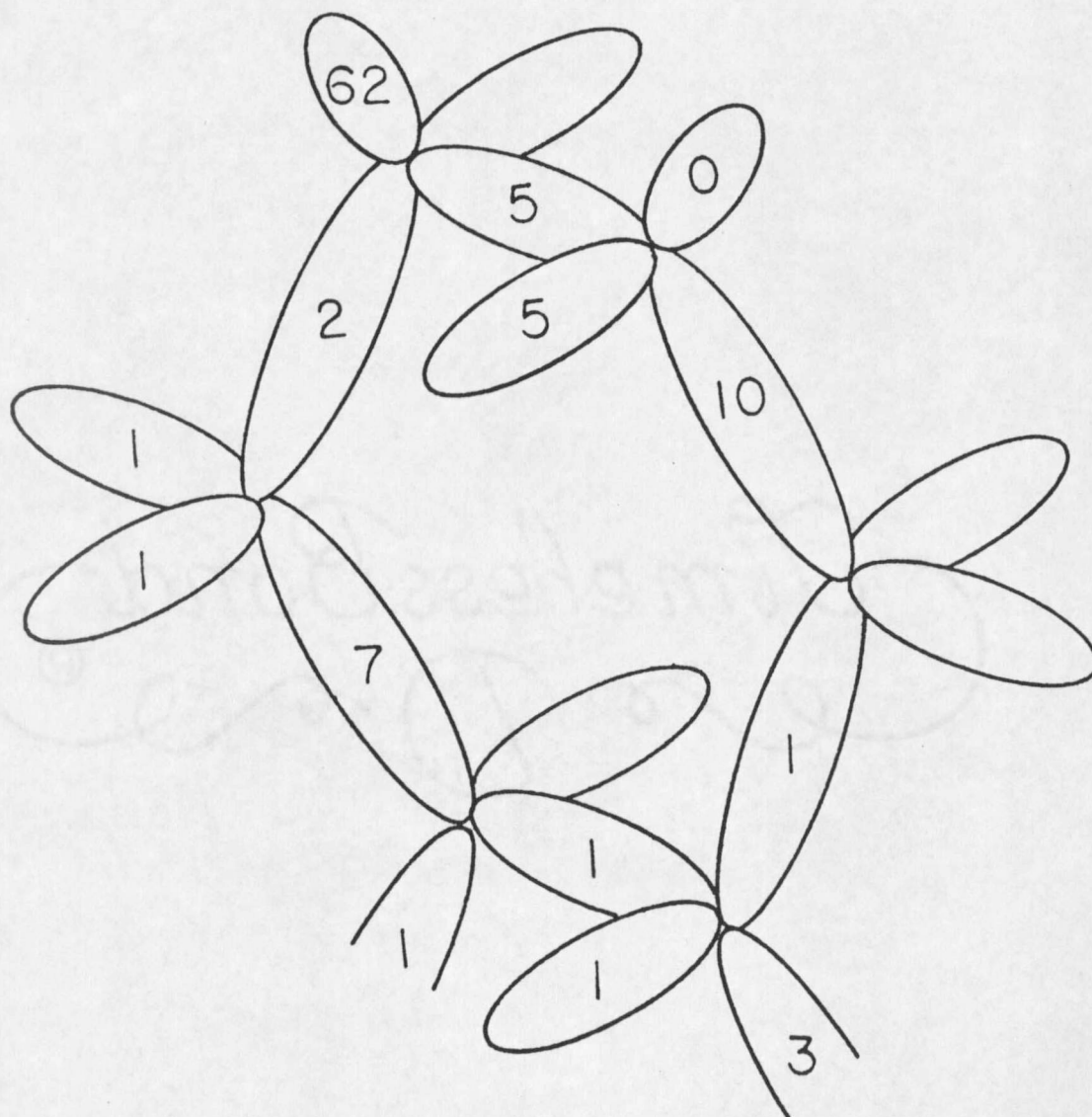


Figure 20. Probability Distribution for an Electron in the B_1 Surface State. Note the large density on the anion dangling hybrid.

continuum at $\bar{M}$, as can be seen in figure 19.

Experimentally, neither the B_1' , nor B_1 are found in the optical gap⁴²⁻⁴⁶. Recent slab calculations by Pandey, Freeouf and Eastman⁹ and others by Chadi¹⁰, all of which include some form of surface relaxation which is not included in the present model, have shown that it is surface relaxation which removes these states from the gap. Knapp^{45,46} has observed that the actual dispersion of the B_1 state seems to be on the order of 1eV, while the dispersion found in both the present calculation as well as in that of Joannopoulos and Cohen is about .4eV. The reason for this discrepancy is not altogether clear, but there is some evidence^{9,10} that it may also be due to surface relaxation.

The probability distribution for state B_2 at the $\bar{M}$ point is shown in figure 21. At $\bar{M}$ there is 70% probability in the parallel bonds, 14% in the cation back bond and 11% in the parallel bonds on the second layer. Thus, this state is localized deeper in the crystal than is the B_1 state. This analysis of the composition of the B_2 state agrees with that of Joannopoulos and Cohen, who refer to it as being composed of parallel bonds along the surface.

In the present calculation, the B_2 surface state is seen to exist in the gap all the way from $\bar{X}'$ to $\bar{X}$. This is not in agreement with Joannopoulos and Cohen who see B_2 die out before it reaches $\bar{X}'$ or $\bar{X}$, or with Chadi or Pandey et al. who find the state at $\bar{X}'$ but not at $\bar{X}$.

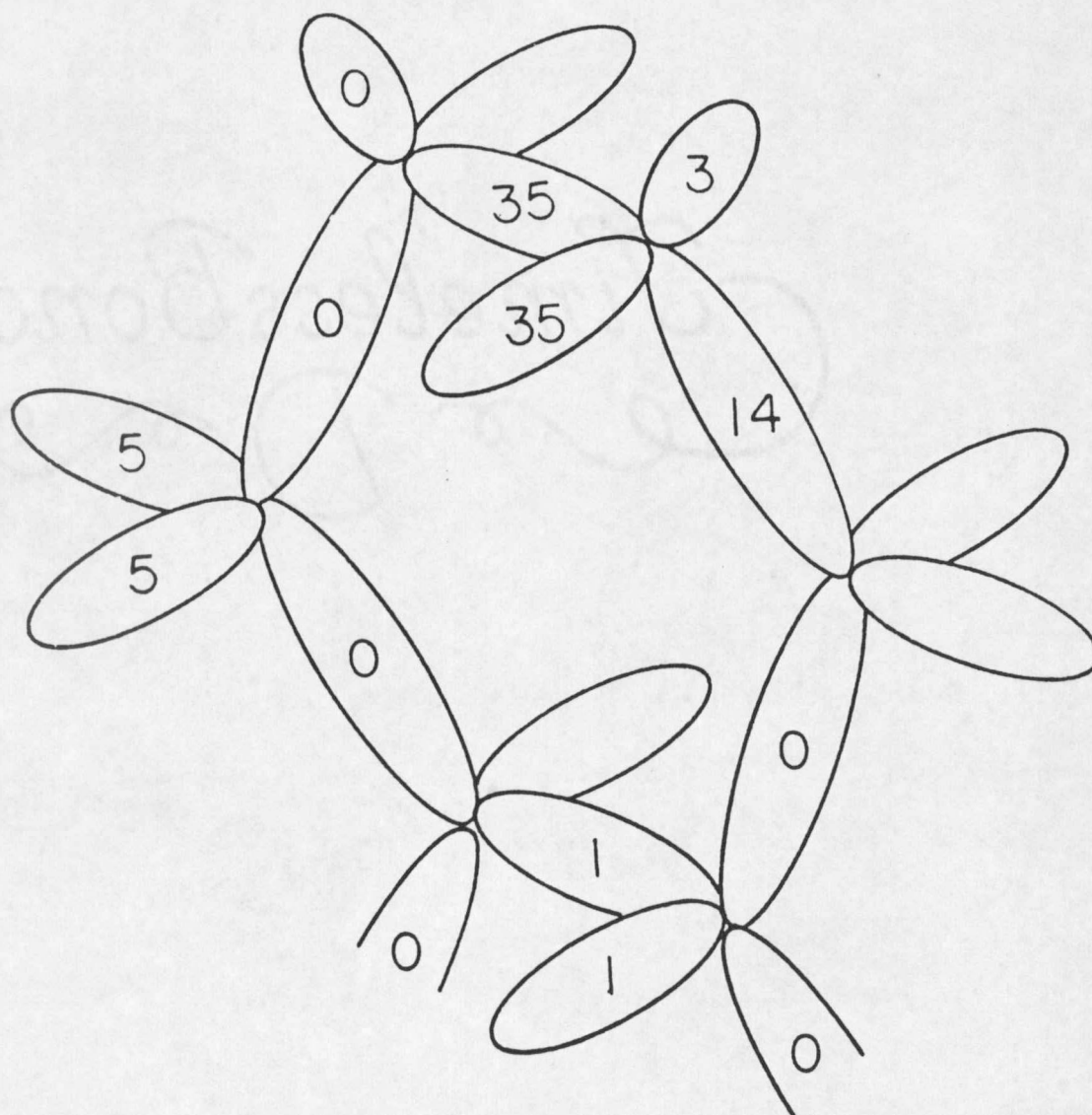


Figure 21. Probability Distribution at $\bar{M}$ for an Electron in the B_2 Surface State.

The binding energies of B_2 at $\bar{X}'$ and at $\bar{X}$ are tiny, being .05 eV and .001 respectively. There is no appreciable localization at these extreme points.

In contrast to the B_2 surface state, the B_3 state exists throughout the entire surface Brillouin zone. Joannopoulos and Cohen have called this state the anion s-like state. Because of the use of bond-orbitals as a basis set, it is difficult to see this in the present model. At the zone center, as represented by figure 22, there is a 41% probability of finding an electron on a parallel bond (that is 20% each), 15% on the anion back bond and 9% on the anion dangling hybrid. This is at least consistent with the notion of an anion s-like state. Total first-layer localization is about 65% and localization on the second layer is about 25%. This state has not been observed in photoemission, which could be due to its s-like character.

Besides the three surface states analyzed above, Chadi¹⁰ has noticed another state in his unrelaxed slab calculation which occurs in the upper part of the zone edge gap near the $\bar{X}'$ point. Chadi, who refers to this surface feature as S_2 , finds that its binding energy and localization are greatly enhanced by relaxation in the several models considered by him^{10,11}. This state also appears in the relaxed models investigated by Pandey et al.⁹.

Although the S_2 surface state appears to be bound in the present, unrelaxed calculation, its binding energy is extremely small and there

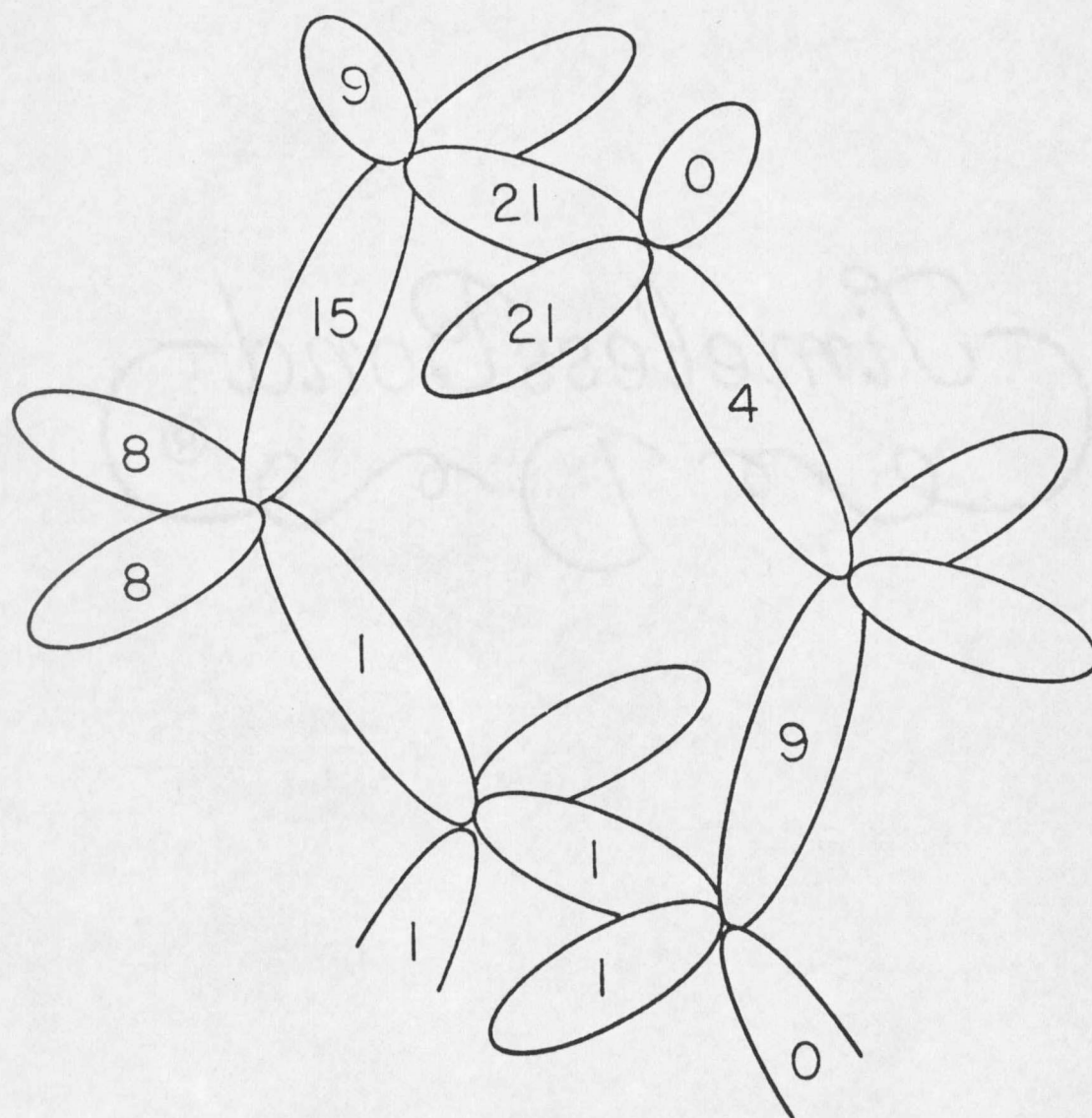


Figure 22. Probability Distribution for an Electron in the B_3 Surface State.

is no recognizable localization. Binding energy of S_2 at $\bar{X}'$ is .004eV. Moving one-fifth of the distance to $\bar{M}$ from $\bar{X}'$ shows that S_2 has joined the upper continuum and there is no longer any trace of S_2 . One reason why other authors including Joannopoulos and Cohen may not have noticed S_2 is because of its small binding energy and poor surface localization. On the other hand, the S_2 state may not appear in their model.

There are many different tight-binding Hamiltonians for the zinc-blende-type semiconductors^{1-6,9-14,32-37}. There are many kinds of ways in which they differ from one another. The essential reason for the proliferation of parameterized Hamiltonians is that the sets of localized atomic functions are immensely over-complete. For example, any function inside the crystal could be expanded in a set of Slater-type orbitals defined with respect to a single site. Three important constraints mitigate this situation: 1) Only a finite number of basis states are retained on each site. 2) Matrix elements between states centered at sites which are separated by more than a certain distance are assumed to vanish. 3) The lack of orthogonality between states on different sites must affect, either explicitly or implicitly, the process of bond formation and the subsequent formation of energy bands. Because of different ways of treating the above constraints, together with differences in choices of bulk band structure, matrix elements which are nominally the same in different parameterized Hamiltonians

may have very different numerical values. In fact, their physical meanings may be entirely different.

Mele and Joannopoulos¹¹ have recently investigated some of the differences between tight-binding Hamiltonians. By studying a collection of nearest-neighbor tight-binding Hamiltonians with four states per site and one with an extra anion 5s state, the above authors have determined that in order to be useful as a tool for investigating surface states this type of Hamiltonian must have the following properties: 1) The diagonal matrix elements of the basis states on each site should be close to the atomic Hartree-Fock value for that state. 2) The other matrix elements must be chosen in such a way as to give a good over-all description of the conduction bands as well as to fit the valence band structure. Criterion 2 was also noted by Chadi¹⁰. Although Mele and Joannopoulos have noted that criterion 1 is intimately related to the change of the overlap between states on neighboring sites for sites at the surface as opposed to sites in the bulk, none of the models which they have examined takes this surface orthogonality correction explicitly into account.

The present calculation may be compared with others appearing in the literature in the following ways. First of all, each of the Hamiltonians discussed by Mele and Joannopoulos^{10,12-14} are nearest-neighbor Hamiltonians. Both the Joannopoulos and Cohen calculation and the present calculation contain more distant interactions. The

unreconstructed model of Pandey et al. also contains some second neighbor interactions. Only two^{10,14} of the models treated by Mele and Joannopoulos produce the correct atomic limit. Chadi's model does. The Hamiltonian of Joannopoulos and Cohen does not. Harrison and Ciraci³⁶ have shown that the atomic energy parameters implicit in the bond-orbital model used in our calculation compare extremely well with the Hartree-Fock energies interpolated from the tables of Herman and Skillman⁴⁷. Finally, among all of the models discussed above only the bond-orbital model takes the change of overlap near the surface explicitly into account.

At this point it must be mentioned that Gregory, Spicer, Ciraci and Harrison³⁷ have applied the bond-orbital model to the (110) surface of GaAs in order to estimate the positions in energy of the dangling hybrid orbital surface states. It is probable that these authors have not performed a slab calculation, as their conclusions are based on the energy positions of the uncoupled hybrid orbitals relative to the bulk band structure. They supposed that the occupied surface state would remain below the valence band maximum, which is not the case.

Another application of the bond-orbital model has been made by Ciraci, Batra and Tiller⁴ who studied the (111) face of zincblende-type semiconductors using a matrix slab method. They have also used the methods of Haydock and Kelly⁴⁸ to compare the surface states which exist on the (111), (110), and (100) surfaces of Si within the

bond-orbital model³⁴.

Unfortunately, the method by which Ciraci, Batra and Tiller have appended the dangling hybrid orbitals to the surface is in error. For this reason, only those surface states on the (111) surface which do not have strong amplitude on the dangling bonds may be expected to be represented correctly by their results.

VI. SUMMARY AND CONCLUSION

A. Generating Function Formalism

The principal thrust of the research presented herein has been to develop and analyze various methods for use in theoretical surface physics. The method of generating functions, as it has been presented above, is an adaptation which facilitates the use of the analytic resolvent method to solve rather realistic tight-binding models of surfaces. In chapters II and III, the method was used to solve models with one or two states per layer, and the solution of these models was discussed in some detail. Generalization of this method to tight-binding models of arbitrary complexity is immediate and will be discussed briefly here.

It may seem reasonable that any tight-binding Hamiltonian may be written in terms of layer orbitals parallel to a given crystal plane. Such a matrix would be of the form

$$H_{\ell\ell'}^{ij}(s_1, s_2), \quad (239)$$

where the subscripts ℓ and ℓ' denote layers and i and j which layer-orbital on layer ℓ and layer ℓ' respectively. s_1 and s_2 are structural factors related to translation in the plane of the layers in complete analogy with (237). Denote by $H_{\ell\ell'}$, the matrix which has (239) as its i,j element. Note that for a tight-binding Hamiltonian, $H_{\ell\ell'}$ is of

finite rank n and is zero when $|\ell - \ell'| > r$ for some range r . When the bulk Green functions are also written in matrix form, then the equations of motion become

$$(1E_{\ell\ell'} - H_{\ell\ell'})G_{\ell'\ell''} = 1\delta_{\ell\ell''}. \quad (240)$$

Because of translation symmetry, $H_{\ell+p,\ell}$ may be written H_p , and likewise $G_{\ell+p,\ell}$ may be written as G_p .

$$\sum_{p=-r}^r (1E_{p0} - H_{-p})G_{\ell+p} = 1\delta_{\ell 0}. \quad (241)$$

The generating function matrix is defined as

$$F(x) = \sum_{\ell} G_{\ell} x^{\ell}. \quad (242)$$

Then, when (241) is multiplied by x^{ℓ} and the result is summed over all layers

$$[1E - H(x)] F(x) = 1, \quad (243)$$

where

$$H(x) = \sum_{p=-r}^r H_p x^p \quad (244)$$

is a finite matrix of rank n .

The determinant of $(E-H)$ is of the form

$$\Delta(x) = \det(1E - H(x)) = a_N \left(x^N + \frac{1}{x^N}\right) + a_{N-1} \left(x^{N-1} + \frac{1}{x^{N-1}}\right) + \dots + a_0, \quad (245)$$

where $N \leq nr$ and the numbers a_N are functions only of E , s_1 and s_2 , as

well as the original tight-binding parameters.

$$\Delta(x) = a_N \frac{1}{x^N} p(x) \quad (246)$$

where $p(x)$ is a monic polynomial of degree $2N$.

The roots of p may be found either in closed form or numerically. The latter is by far the more powerful method of practical use⁷⁻⁸, while the former divided tight-binding models which can in principle be solved in terms of elementary functions from those which cannot. This is because the other steps required to produce surface Green functions require only a finite number of arithmetic operations, though this number may be quite large indeed.

There exists a solution of a given tight-binding model surface problem in closed form in terms elementary functions if and only if the Hamiltonian is such that p is solvable. Due to the parametric dependence upon complex s_1 , s_2 and E of the coefficients of p , cases of solvable p with degree more than four must be very exceptional.

Denoting the roots of p by x_k , the generating function matrix may now be written in the form

$$F(x) = \frac{U(x)}{p(x)} = \sum_k \frac{U(x_k)}{(x-x_k) p'(x_k)}. \quad (247)$$

There is also the possibility that $F(\infty) \neq 0$, but this is very unphysical and may be ignored in this summary.

After Laurent series expanding F , the Green functions may be read

as the coefficients of the expansion and their general form is

$$G_{\ell}^{ij} = \sum_k t_k^{ij} x_k^{|\ell|} \quad (248)$$

where the t_k^{ij} are residues from (247), and k of the summation runs only over those roots of p such that $|x_k| < 1$. Unfortunately t_k^{ij} may depend upon the sign of ℓ .

All of this has been illustrated in chapters II and III. As another illustration of the kinds of results which may be obtained from the bulk Green function, figure 23 presents the total bulk layer density of states produced in this way from the same Hamiltonian used in chapter VI for the thin film of GaAs. The various curves of figure 23 indicate densities at different values of the x component of $\vec{k}_{||}$, corresponds to different values of s_1 .

Once the bulk Green functions are obtained from the generating function matrix, the surface problem may be solved from the relation

$$J = (1 - GV)^{-1}G. \quad (249)$$

In most cases, the Shockley surface is of interest and then

$$J_{AA} = G_{AA} - G_{AB}(G_{BB}^{-1})G_{BA}, \quad (250)$$

where A is inside the crystal and B is a barrier region, as explained in chapter II.

The method of generating functions as outlined in this summary is a formal refinement of the analytic resolvent method used by Davison

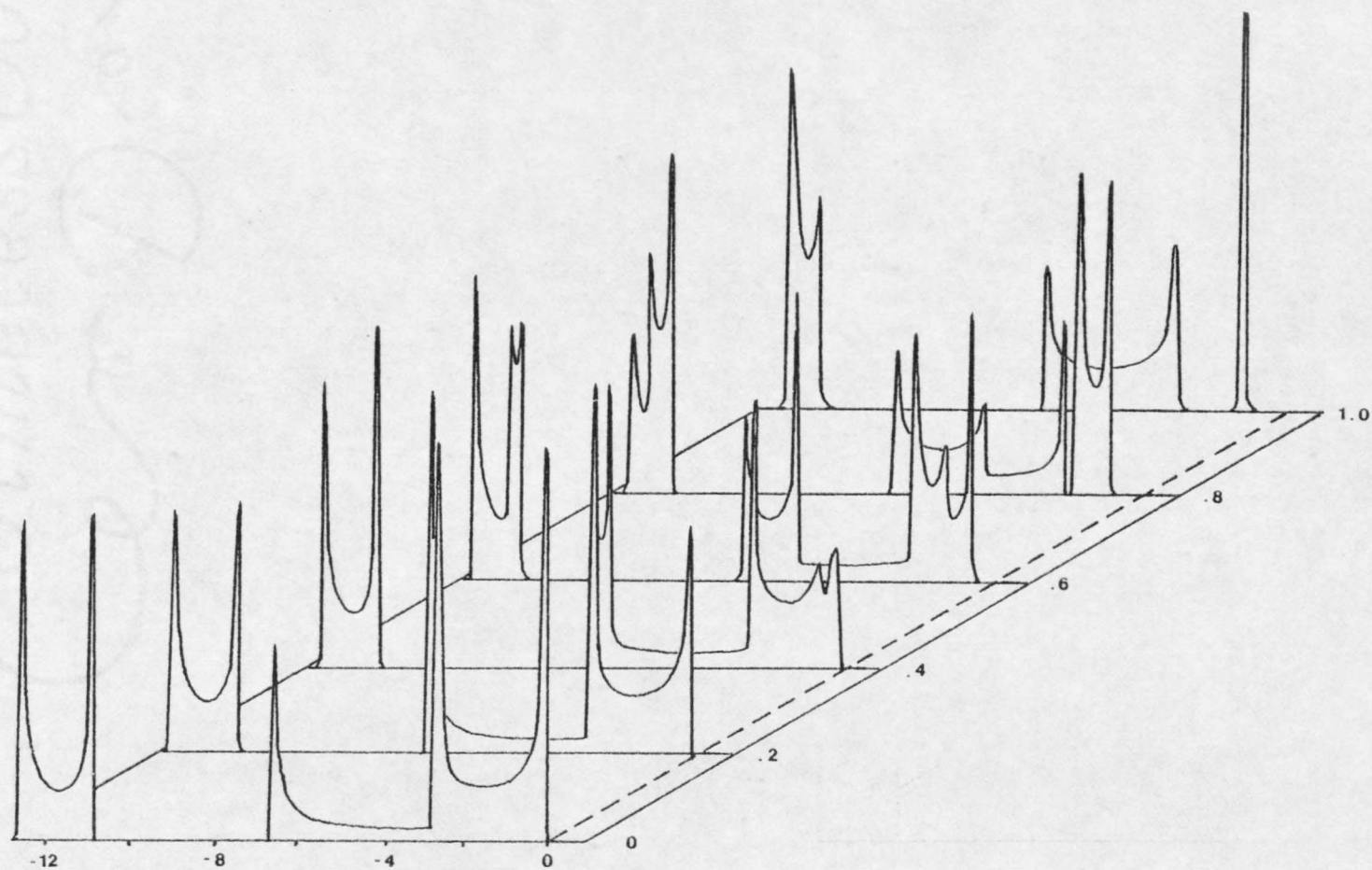


Figure 23. Bulk Layer Density of States for GaAs (110) as a Function of Energy in eV and k in Units of the $\bar{\Gamma}-\bar{X}'$ Distance.

and Levine¹⁶ and developed by Freeman²¹. Since the generating function formalism is intrinsically integration free, many of the confusions arising in the Fourier transform formulations are circumvented.

It may be noted that the generating function for the Green function in the presence of the surface could be found directly, thus bypassing the bulk Green function. However, because the bulk problem is itself interesting and because of the ease with which, through equation (249), one may change the surface potential, it is usually better to calculate the bulk Green function first.

The ease with which the layer densities of states may be factored according to layer orbital, as pointed out in chapter II, is illustrated again in figure 24 where the s-like part of the surface layer densities of the two-band problem treated in that chapter are presented. These curves should be compared with those of figure 7 where the total densities on the first three layers were presented.

Using the generating function method, several model calculations have been performed, including the one and two-band models of chapter II and III. A number of important qualitative results have been discovered in this way.

The standing-wave features in the layer densities of states which were pointed out in chapter II and III and which are also obvious in figure 24 have been observed before²³. But, it is now seen that these are always present and that they arise because of the replacement of

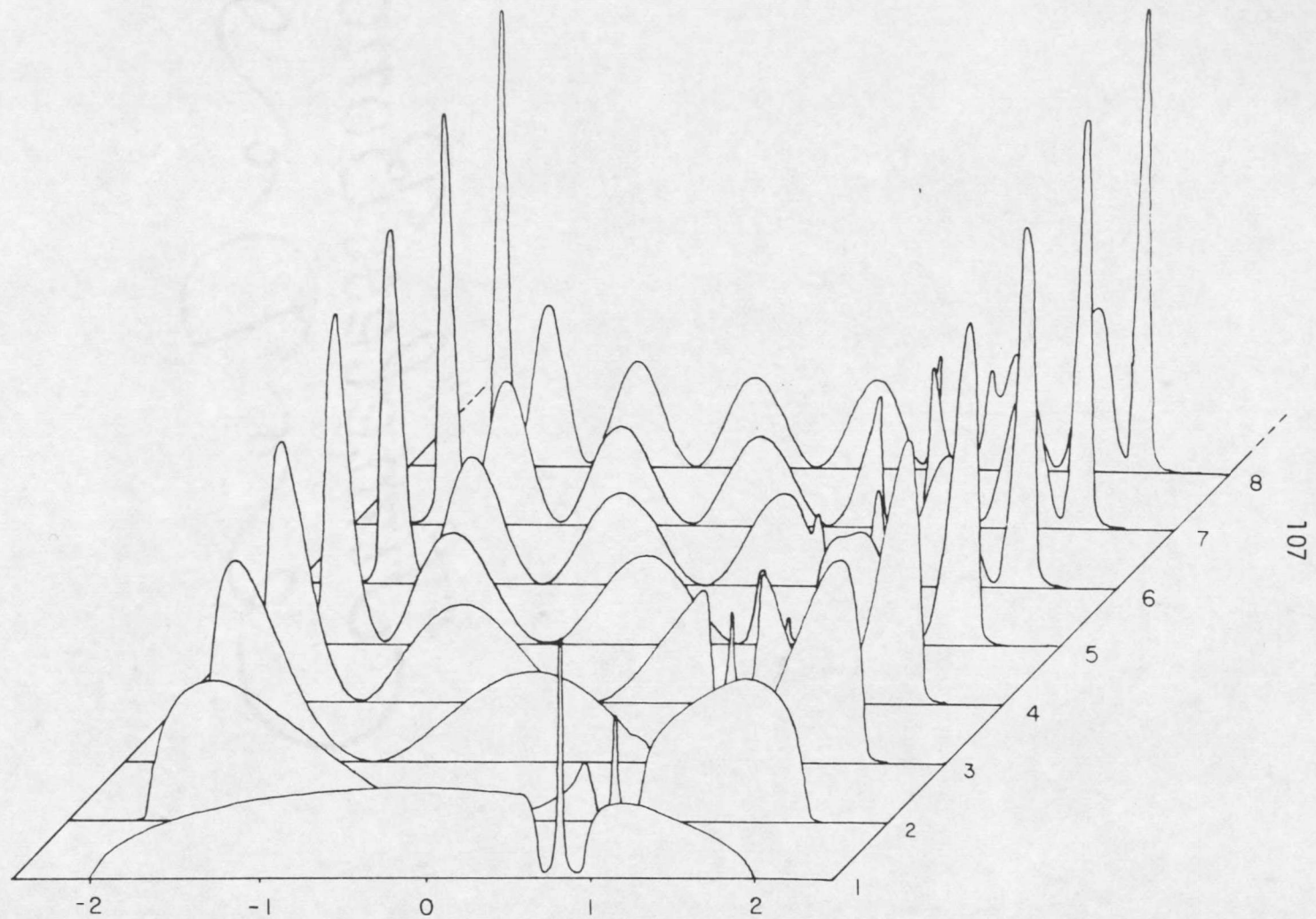


Figure 24. s-like Part of the Layer Densities for the Model of Chapter III.

the periodic boundary conditions of the bulk by standing-wave boundary conditions.

Shockley had discovered that there are surface states which arise due to the formation of hybridization gaps³⁰. These states occur in the s-p model at exactly the point in energy where the unhybridized bands would have crossed. The existence of such a state does not depend, in the s-p model, upon the strength of the hybridization. As the gap becomes narrow, the gap state is only weakly localized. Using the generating function method, Kawajiri⁴⁹ has found that there is no similar gap state in the s-d model. The only difference between the s-p and the s-d models is that the s-p interaction matrix element is odd with respect to site interchange while the corresponding s-d matrix element is even.

$$\begin{aligned} \langle s\ell | H | p\ell' \rangle &= - \langle p\ell | H | s\ell' \rangle \\ \langle s\ell | H | d\ell' \rangle &= + \langle d\ell | H | s\ell' \rangle. \end{aligned} \tag{251}$$

It is not known at this point whether this parity difference is necessary in order to produce a gap state, so that there can be no state in an s-d gap until some odd parity state is mixed in, or whether the addition of second neighbor interactions might also produce a state in a strictly even parity gap. This should be investigated.

In fact, the simplicity of the generating function method makes it important as a formal, mathematical tool. We have used it, for example, to determine a criterion for solvability for tight-binding

Hamiltonians. At the heart of the solution for any semi-finite tight-binding model is a characteristic polynomial. This polynomial, which has been discussed above and also in the Introduction, is the characteristic polynomial for the difference equations; the homogeneous solutions to which are the eigenvectors of the Hamiltonian, and the impulse solutions to which are the Green functions. The various exact methods of solution must all arrive at this same polynomial, and the solution must be expressed in terms of its roots. This close relationship between the various methods has been demonstrated in chapter II for several methods which include most of the popular methods to be found in the literature.

The Green function method was used in chapter III to produce the exact solution to a two-band model and this solution in turn was used to investigate the validity of a simple bond-orbital model. Bond-orbital models are extremely useful in semiconductor studies because the number of basis functions is cut in half and the number of tight-binding basis functions is considerably reduced. Perhaps more importantly, the bond-orbitals seem to be a physically meaningful basis for the representation of the filled valence bands of semiconductors.

B. Thin Film Calculation

The large matrix method which has often been applied to the problem of finding the eigenstates of a thin film is also a method of

solving the system of difference equations for the model. In this method, however, the boundary conditions are different. There must be standing wave boundary conditions at each side of a finite region, and this makes the spectrum discrete. It also makes the solution more difficult formally, but quite simple numerically.

When the bond-orbital model of Harrison was used for a twelve layer slab of gallium arsenide, the numerical solution became rather neat. The results are in excellent agreement with those of Joannopoulos and Cohen who did a similar computation for the unrelaxed (110) surface of GaAs, but without making the bond-orbital approximation. This successful result is an important confirmation of the validity of the bond-orbital model as a tool for the investigation of surfaces. The bond-orbital basis is founded on bulk chemistry and it was not known whether this extremely simple model with only three parameters could be used at the surface, even taking the overlap correction into account. As we have seen in the simpler model, the surface potential mixes and bonding and anti-bonding states. But, it seems that this mixing must be quite negligible in the case of the (110) surfaces of zincblende-type semiconductors.

Although a bond-orbital calculation for the (111) surfaces of GaAs and of Si has been carried out by Ciraci, Batra and Tiller⁴, these authors have made an error which invalidates the results to some extent. Their results look quite reasonable in themselves, but rather

than ignoring the bonding-antibonding matrix elements, these authors have done what formally amounts to neglecting some second neighbor hybrid-orbital matrix elements near the surface. They are not at liberty to do this, however, within the context of the bond-orbital model. Thus, no fair tests have appeared up to now which permit an assessment of the use of a bulk bond-orbital model in this way. The results presented above, however, do provide for such judgment.

Harrison has used the bond-orbital concept in rather a different way to investigate surface reconstruction³³. By using a full hybrid-orbital basis set near the surface and then rehybridizing this set to form surface bond-orbitals, Harrison is able to compute a binding energy difference as a function of surface atom position. This use of the bond-orbital concept actually transcends the simple bulk model with few parameters.

Whether or not the bulk model may be used as it stands to predict surface relaxation effects on the electronic structure by simply neglecting the bonding-antibonding part of the perturbation is not clear. It is also not known at this time whether chemisorption might be treated using only a bond-orbital basis set if, for example, the one, important adsorbate energy level lies deep within the substrate valence bands.

The bond-orbital picture of the GaAs (110) surface states is easily related to a ball-and-stick model of the crystal structure. This

picture is possible because of the role played by the filled valence bands in the crystal bonding. This intimate connection of the bond-orbitals with the valence bands is in turn responsible for the failure of the model to correlate the properties of the empty states. Tight-binding models in general do not represent the conduction bands very well, and after the bonding-antibonding interaction is neglected, there is very little chance of representing the conduction bands in terms of antibonding orbitals only³⁵⁻³⁶.

The results obtained using the model of Harrison for the zinc-blende semiconductors are encouraging, and it should be interesting to create a similar bond-orbital for other types of semiconductors and to use this model to investigate the surface electronic properties.

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APPENDIX A

Bulk matrix elements of the bond-orbital model of Harrison for zincblende semiconductors are presented here.

1. $\langle 1, \ell' m' n' | H | 1, \ell m n \rangle = \epsilon_b \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n} - B_4 [\delta_{\ell' \ell} \delta_{m' m} (\delta_{n' n+1} + \delta_{n' n-1}) + \delta_{\ell' \ell} (\delta_{m' m-1} \delta_{n' n+1} + \delta_{m' m-1} \delta_{n' n+1}) + \delta_{\ell' \ell-1} \delta_{m' m-1} \delta_{n' n+2} + \delta_{\ell' \ell+1} \delta_{m' m+1} \delta_{n' n-2}]$.
2. $\langle 1, \ell' m' n' | H | 2, \ell m n \rangle = -B_1^C \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n} - B_1^A \delta_{\ell' \ell+1} \delta_{m' m+1} \delta_{n' n-2}$.
3. $\langle 1, \ell' m' n' | H | 3, \ell m n \rangle = -B_1^C \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n} - B_1^A \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n-1}$.
4. $\langle 1, \ell' m' n' | H | 4, \ell m n \rangle = -B_1^C \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n} - B_1^A \delta_{\ell' \ell} \delta_{m' m+1} \delta_{n' n-1}$.
5. $\langle 2, \ell' m' n' | H | 2, \ell m n \rangle = \epsilon_b \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n} - B_4 [\delta_{\ell' \ell-1} \delta_{m' m-1} \delta_{n' n+1} + \delta_{\ell' \ell+1} \delta_{m' m+1} \delta_{n' n-1} + \delta_{m' m} (\delta_{\ell' \ell-1} \delta_{n' n+1} + \delta_{\ell' \ell+1} \delta_{n' n-1}) + \delta_{\ell' \ell-1} \delta_{m' m-1} \delta_{n' n+2} + \delta_{\ell' \ell+1} \delta_{m' m+1} \delta_{n' n-2}]$.
6. $\langle 2, \ell' m' n' | H | 3, \ell m n \rangle = -B_1^C \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n} - B_1^A \delta_{\ell' \ell-1} \delta_{m' m-1} \delta_{n' n+1}$.
7. $\langle 2, \ell' m' n' | H | 4, \ell m n \rangle = -B_1^C \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n} - B_1^A \delta_{\ell' \ell-1} \delta_{m' m} \delta_{n' n+1}$.
8. $\langle 3, \ell' m' n' | H | 3, \ell m n \rangle = \epsilon_b \delta_{\ell' \ell} \delta_{m' m} \delta_{n' n} - B_4 [\delta_{\ell' \ell} \delta_{m' m} (\delta_{n' n+1} + \delta_{n' n-1}) + \delta_{\ell' \ell+1} \delta_{m' m+1} \delta_{n' n-1} + \delta_{\ell' \ell-1} \delta_{m' m-1} \delta_{n' n+1} + \delta_{\ell' \ell} \delta_{n' n} (\delta_{m' m+1} + \delta_{m' m-1})]$.

$$9. \langle 3, \ell' m' n' | H | 4, \ell mn \rangle = -B_1^C \delta_{\ell, \ell} \delta_{m, m} \delta_{n, n} - B_1^A \delta_{\ell, \ell} \delta_{m, m+1} \delta_{n, n}.$$

$$10. \langle 4, \ell' m' n' | H | 4, \ell mn \rangle = \epsilon_b \delta_{\ell, \ell} \delta_{m, m} \delta_{n, n} - B_4 [\delta_{\ell, \ell} \delta_{m, m+1} (\delta_{n, n} + \delta_{n, n-1}) \\ + \delta_{\ell, \ell} \delta_{m, m-1} (\delta_{n, n} + \delta_{n, n+1}) + \delta_{m, m} (\delta_{\ell, \ell+1} \delta_{n, n-1} + \delta_{\ell, \ell-1} \delta_{n, n+1})].$$

APPENDIX B

Matrix elements are presented for the Hamiltonian of Appendix A in terms of layer orbitals built on (110) planes.

1. $\langle 1, m | H | 1, n \rangle = \epsilon_b \delta_{mn} - B_4 [(\delta_{mn+2} + \delta_{mn-2}) + (s_2 + 1/s_2)(\delta_{mn-1} s_1 + \delta_{mn+1}/s_1)]$.
2. $\langle 1, m | H | 2, n \rangle = -B_1^C \delta_{mn} - B_1^A \delta_{mn-2}$.
3. $\langle 1, m | H | 3, n \rangle = -B_1^C \delta_{mn} - B_1^A \delta_{mn-1} s_1 s_2$.
4. $\langle 1, m | H | 4, n \rangle = -B_1^C \delta_{mn} - B_1^A \delta_{mn-1} s_1 / s_2$.
5. $\langle 2, m | H | 2, n \rangle = \epsilon_b \delta_{mn} - B_4 [(\delta_{mn+2} + \delta_{mn-2}) + (s_2 + 1/s_2)(s_1 \delta_{mn+1} + \delta_{mn-1}/s_1)]$.
6. $\langle 2, m | H | 3, n \rangle = -B_1^C \delta_{mn} - B_1^A \delta_{mn+1} s_1 s_2$.
7. $\langle 2, m | H | 4, n \rangle = -B_1^C \delta_{mn} - B_1^A \delta_{mn+1} s_1 / s_2$.
8. $\langle 3, m | H | 3, n \rangle = \epsilon_b \delta_{mn} - B_4 [(s_2^2 + 1/s_2^2) \delta_{mn} + (s_1 s_2 + 1/s_1 s_2)(\delta_{mn+1} + \delta_{mn-1})]$.
9. $\langle 3, n | H | 4, n \rangle = -B_1^C \delta_{mn} - B_1^A \delta_{mn} / s_2^2$.

$$\begin{aligned}
 10. \quad \langle 4, n | H | 4, n \rangle = & \varepsilon_b \delta_{mn} - B_4 [(s_2^2 + 1/s_2^2) \delta_{mn} \\
 & + (s_1/s_2 + s_2/s_1) (\delta_{mn+1} + \delta_{mn-1})].
 \end{aligned}$$

APPENDIX C

The matrix elements required in the thin film calculation are given here in terms of the bulk-to-surface coupling coefficients listed in the text and illustrated in figure 14.

1. $\langle 0|H|2\rangle = g_4 s_1 (s_2 + 1/s_2)$
2. $\langle 0|H|3\rangle = g_3 s_1 s_2$
3. $\langle 0|H|4\rangle = g_3 s_1 / s_2$
4. $\langle 0|H|5\rangle = g_3$
5. $\langle 0|H|6\rangle = g_4$
6. $\langle 1|H|2\rangle = g_1$
7. $\langle 1|H|3\rangle = g_1$
8. $\langle 1|H|4\rangle = g_1$
9. $\langle 1|H|5\rangle = g_2 (s_2 + 1/s_2) / s_1$
10. $\langle 1|H|9\rangle = g_2$
11. $\langle 4N|H|4N+1\rangle = g_3 s_2 / s_1$
12. $\langle 4N-1|H|4N+1\rangle = g_3 / (s_1 s_2)$
13. $\langle 4N-3|H|4N+1\rangle = g_4 (s_2 + 1/s_2) / s_1$
14. $\langle 4N-6|H|4N+1\rangle = g_3$
15. $\langle 4N-7|H|4N+1\rangle = g_4$
16. $\langle 4n-2|H|4N\rangle = g_1$

$$17. \quad \langle 4N-2 | H | 4N-1 \rangle = g_1$$

$$18. \quad \langle 4N-3 | H | 4N-2 \rangle = g_1$$

$$19. \quad \langle 4N-10 | H | 4N-2 \rangle = g_2$$

$$20. \quad \langle 4N-6 | H | 4N-2 \rangle = g_2(s_2 + 1/s_2)s_1$$

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