

EFFECTIVE SURFACE POTENTIAL METHOD FOR CALCULATING SURFACE STATES*

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A novel formalism (the effective surface potential method) is developed for calculating surface states. Like the Green function method of Kalkstein and Soven and the transfer matrix method of Falicov and Yndurain, the technique is exact for simple tight binding Hamiltonians. As well as offering an alternative viewpoint, the present method provides a simple analytic expression describing the surface states. At each point \mathbf{k}_s in the surface Brillouin zone the semi-infinite solid is viewed as an effective linear chain where each element of the chain is a planar layer. The solution to the linear chain problem can be expressed in terms of an effective potential $h(\mathbf{k}_s, E)$ at each energy E . A number of examples are presented in detail; “sp^d” Hamiltonians for a linear chain ($d = 1$), the honeycomb lattice ($d = 2$), the 111 surface of silicon ($d = 3$), and a dissected Bethe lattice. Various exact results are given, e.g. the extremities of surface state bands and the surface density of states of p-like (delta function) bands. The results of Kalkstein and Soven for the 100 surface of a simple cubic solid with a perturbation on the surface layer are rederived.

1. Introduction

There has recently been a considerable amount of effort, both experimental and theoretical, to develop an understanding of the electronic properties of surfaces from a basic viewpoint. Much of this effort has been directed toward understanding the Si 111 surface. The most elaborate and successful calculations are those of Ap-

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Appelbaum and Hamann [1] who have performed fully self-consistent pseudopotential calculations, allowing for surface relaxation and charge redistribution. Similar results have been achieved by Pandey and Phillips [2], who use a semi-empirical tight binding Hamiltonian and 8 parameter. These parameters are chosen so that the bulk band structure of Si, using pseudopotentials, is reproduced as well as possible. Pandey and Phillips use finite thicknesses (~ 20 atomic layers) in order to facilitate the calculations. Their results are most readily expressed in terms of a local density of states but they can also extract the surface dispersion curves. Similar calculations have been done by Chadi and Cohen [3].

These calculations suggest that many of the features of surface states do not depend on the precise details of these calculations or the model used (e.g., whether there is a surface state in the band gap). With this in mind we decided to investigate some *simple model Hamiltonians* of the tight binding kind using simple but exact techniques based on what we shall call the *effective potential method*. We have been able to find algebraic expressions for a number of quantities. However, inasmuch as our results are significantly different from those of Appelbaum and Hamann [1], and Pandey and Phillips [2], it appears that only *some* aspects of the surface problem are governed by general considerations, whilst many others are extremely sensitive to both the model and to surface reconstruction. Nevertheless, we feel the method is of fairly general application and we present it here together with a number of examples of its use. In addition, we plan to apply the method to the calculation of vibrational states near the Si 111 surface. Simple force constant models are quite realistic in this case and the results may be less sensitive to surface reconstruction. After this work was substantially complete, we became aware of work on 111 surfaces of Si and Ge that uses the transfer matrix method by Falicov and Yndurian [4] which we will abbreviate by FY.

Like the Green function method of Kalkstein and Soven (KS) and the transfer matrix method of FY, the effective surface potential method is exact for simple tight binding Hamiltonians. However, they differ not only conceptually but also in their calculating procedures. In the KS method the semi-infinite crystal is formed by passing an imaginary cleavage plane in some crystallographic direction of the infinite crystal. The hopping integrals which couple the two cleaved half-crystals are set equal to zero. The difference between the cleaved half-crystals and the infinite crystal Hamiltonians is then treated as a scattering potential. Thus the Green function for the cleaved half-crystals can be expressed in terms of the bulk Green function and the scattering potentials introduced by the cleavage plane. On the other hand, the FY method is closely related to the conventional LCAO method in which a set of equations of motion has to be solved simultaneously. As pointed out by FY themselves, their method, which involves a repetitive procedure, is straightforward, but long and cumbersome [4]. In comparison, the effective surface potential method outlined in this paper provides a very simple, transparent and concise analytic expression for the surface Green function.

The layout of the paper is as follows. In the next section we describe how a linear

chain may be solved using the effective potential method. In section 3, the result of Kalkstein and Soven for a simple cubic 100 surface with a localized perturbation is rederived. In the following two sections we do calculations for unreconstructed surfaces in the two-dimensional honeycomb lattice and the 111 surface of Si. Some aspects of these calculations become clearer when the surface states on a Bethe lattice are calculated in section 6. Although this is an artificial lattice, it has some simple and intriguing properties that relate to the calculations for both the honeycomb and diamond cubic lattices.

2. Linear chains

As a preliminary to considering a linear chain with two kinds of interactions, we first consider a simple monatomic chain with nearest neighbor interaction V described by the Hamiltonian:

$$H = - \sum_i V|i\rangle\langle i+1| + \text{h.c.} \quad (1)$$

The density of states may be obtained most easily from the Green function operator:

$$G = (E - H)^{-1}. \quad (2)$$

The local density of states at the i th atom is then given by:

$$\rho_{ii}(E) = -\frac{1}{\pi} \text{Im} \langle i|G|i\rangle, \quad (3)$$

where E has a small positive imaginary part. The Green function for this system may be written:

$$G = \begin{pmatrix} E & V & 0 & 0 & \dots \\ V & E & V & 0 & \dots \\ 0 & V & E & V & \dots \\ 0 & 0 & V & E & \dots \\ \dots & \dots & \dots & \dots & \dots \end{pmatrix}, \quad (4)$$

using (1) and (2). The atoms are labelled from 0 to ∞ with the 0th atom being the surface atom. The Green function at the surface may be written as:

$$g = \langle 0|G|0\rangle_s = 1/(E - h), \quad (5)$$

where $h(E)$ is a self-energy representing the one-sided chain. It is clear that for an atom in an infinite system the bulk Green function would be

$$g' = \langle 0|G|0\rangle_B = 1/(E - 2h), \quad (6)$$

because there is a self-energy for both the left and right pieces of the chain, starting from a single atom. Eqs. (5) and (6) show that the Green function for a surface and bulk atom are related in the linear chain by

$$2/g = 1/g' + E. \quad (7)$$

The effective potential h can be calculated directly from (4) and (5):

$$g = \frac{1}{E - h} = \left(\begin{array}{cc} E & V \\ V & E - h \end{array} \right)_{00}^{-1}. \quad (8)$$

Eliminating h :

$$g = \left(\begin{array}{cc} E & V \\ V & g^{-1} \end{array} \right)_{00}^{-1}, \quad (9)$$

from which we get a quadratic equation for g :

$$(Vg)^2 - 2\alpha(Vg) + 1 = 0, \quad (10)$$

with

$$\alpha = E/2V. \quad (11)$$

We therefore obtain:

$$g = [\alpha \pm (\alpha^2 - 1)^{1/2}] / V, \quad (12)$$

where the ambiguity in the \pm signs is removed by requiring that:

$$\text{Im}(g) < 0 \text{ for values of } E \text{ slightly above the real axis.} \quad (13)$$

There is no surface state in (12) as the density of states lies entirely within the bulk band defined by $|\alpha| \leq 1$. Note that by inserting eq. (12) into eq. (7) we obtain the usual bulk Green function:

$$g' = \pm 1/2V(\alpha^2 - 1)^{1/2}, \quad (14)$$

where again the ambiguity in sign is removed by applying the condition (13).

The Green functions for all the other atoms may be found easily by noticing that because of the condition (9) we may terminate the continued fraction at any level so that:

$$g = \left(\begin{array}{cc} E & V \\ V & g^{-1} \end{array} \right)_{00}^{-1} \equiv \left(\begin{array}{ccc} E & V & 0 \\ V & E & V \\ 0 & V & g^{-1} \end{array} \right)^{-1} \equiv \left(\begin{array}{cccc} E & V & 0 & 0 \\ V & E & V & 0 \\ 0 & V & E & V \\ 0 & 0 & V & g^{-1} \end{array} \right)^{-1}, \quad (15)$$

and that for example

$$\langle 1|G|1\rangle = \begin{pmatrix} E & V \\ V & g^{-1} \end{pmatrix}_{11}^{-1} \equiv \begin{pmatrix} E & V & 0 \\ V & E & V \\ 0 & V & g^{-1} \end{pmatrix}_{11}^{-1}. \tag{16}$$

A little algebra will convince the reader that

$$\langle n|G|n\rangle = g' \left[1 + \left(\frac{Eg' - 1}{Eg' + 1} \right)^n \frac{(1 - Eg')}{(1 + Eg')} \right]. \tag{17}$$

This expression reduces to the bulk Green's function g' as $n \rightarrow \infty$ and to the surface Green function $g = 2g'/(1 + Eg')$ when $n = 0$.

These ideas can be easily generalized to more complex linear chain systems. For example, fig. 1 shows a chain with two kinds of interactions, V_1 (which might represent s-p splitting on a single atom) and V (which might represent a bonding-antibonding interaction). The Hamiltonian for this system is:

$$H = - \sum_i [V_1|2i\rangle\langle 2i + 1| + V|2i - 1\rangle\langle 2i|] + \text{h.c.} \tag{18}$$

A simple generalization of eq. (9) leads to a self-consistent equation for the Green function g at the surface site

$$g = \begin{pmatrix} E & V_1 & 0 \\ V_1 & E & V \\ 0 & V & g^{-1} \end{pmatrix}_{00}^{-1}. \tag{19}$$

Since the number of states in the unit cell has increased from 1 to 2 states, the corresponding self-consistency condition for g has increased from one involving a 2×2 matrix to one involving a 3×3 matrix. Notice, however, that because g^{-1} only occurs in the lower right hand corner of (19) we still get a quadratic equation for g , and the solutions (12) and (14) are identical to (12) if α is replaced by:

$$\alpha = (E^2 + V^2 - V_1^2)/2EV. \tag{20}$$

One notices that α has a pole at $E = 0$ which implies the existence of a surface state at that energy provided that the residue of the Green's function is non-zero. The condition (13) implies that this happens only if $V_1/V < 1$, which is the so-called Shockley [5] state shown in fig. 2.

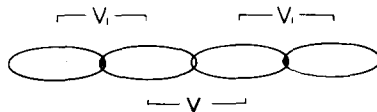


Fig. 1. A linear chain with two states/atom. The interaction V_1 represents the s-p splitting on a single atom (denoted by a solid circle) and the interaction V separates the bonding/antibonding states.

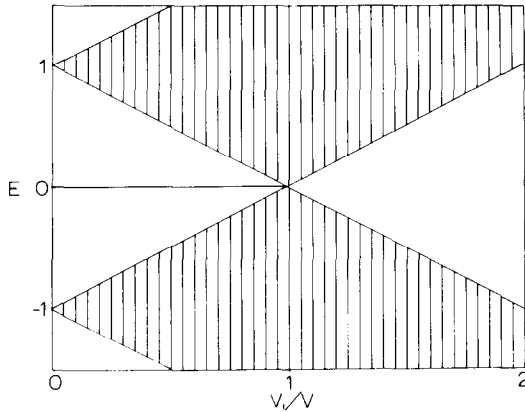


Fig. 2. The allowed energies for the chain shown in fig. 1. The bulk bands are shown together with the Shockley state at $E = 0$ for $V_1/V < 1$. The energy is measured in units of V .

3. Simple cubic 100 surface

The method we have developed can be illustrated most easily for the case of the 100 surface of a simple cubic material. We use a simple tight binding Hamiltonian:

$$H = -V \sum_{\langle i\delta \rangle} |i\rangle \langle i + \delta|, \tag{21}$$

where i goes over all the sites and δ goes over all the neighbors of i and the brackets $\langle \rangle$ mean no double counting. The wave vector parallel to the surface \mathbf{k}_s can still be used to classify states and so we may regard the present problem as being formally equivalent to a linear chain problem *at each* \mathbf{k}_s . The effective linear chain has a Hamiltonian like (1) but with an additional diagonal term:

$$-2V [\cos k_x a + \cos k_y a], \tag{22}$$

that arises from the interaction of an atom with its four neighbors within a plane (the z axis is perpendicular to the surface and the nearest neighbor separation is a). We have put $\mathbf{k}_s = (k_x, k_y)$. The Green function G [analog of eq. (4)] becomes:

$$G = \begin{pmatrix} E+2V(\cos k_x a + \cos k_y a) & V & 0 & 0 \\ V & E+2V(\cos k_x a + \cos k_y a) & V & 0 \\ 0 & V & E+2V(\cos k_x a + \cos k_y a) & V \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix} \tag{23}$$

and the self-consistent equation for g [analog of eq. (9)] becomes:

$$g = \begin{pmatrix} E + 2V(\cos k_x a + \cos k_y a) & V \\ V & g^{-1} \end{pmatrix}_{00}^{-1} \quad (24)$$

which has the solution given by eqs. (10) and (11) with:

$$\alpha = [E + 2V(\cos k_x a + \cos k_y a)]/2V. \quad (25)$$

Eqs. (5)–(13) still hold as long as we apply them at a particular \mathbf{k}_s , and make the replacement

$$E \rightarrow E + 2V(\cos k_x a + \cos k_y a). \quad (26)$$

Now suppose an extra diagonal potential U is placed on the surface atoms only. The new surface Green function g_u is related to the old one (with U switched off) via the Dyson equation, i.e.,

$$g_u = g + gUg_u, \quad g_u = 1/(g^{-1} - U). \quad (27)$$

Using the result (17) for $\langle 0|G|0 \rangle = g$, we find that:

$$g_u = g' \left[1 + \frac{1 - (E - 2U)g'}{1 + (E + 2U)g'} \right]. \quad (28)$$

This result is the same as found by Kalkstein and Soven [6] [eq. (2.20)]. The Green functions away from the surface in the presence of the perturbation U may be found in a similar way.

All the basic principles of the method of calculation have been illustrated in this section. The calculation has three parts:

- (a) The solid is sliced into planes so that an effective linear chain can be defined for each surface wave vector \mathbf{k}_s .
- (b) The bulk information is summed up in a Green function for each \mathbf{k}_s .
- (c) A finite matrix is set up that is terminated *outside* the range of reconstruction by the inverse Green function found in (b).

The 100 surface of the simple cubic lattice is sufficiently simple that the method is of no advantage. However, in more complex geometries such as those discussed in the next two sections, it provides a very compact way of approaching the problem.

4. The honeycomb lattice

A more complex geometrical arrangement is provided by the honeycomb lattice, a portion of which is shown in fig. 3. The Hamiltonian is constructed from “sp²” orbitals labelled $|ij\rangle$, where i denotes the atom and j the bond. Three directed orbitals such as those labelled 1, 2, 3 in fig. 3 can be formed at each atom. The Hamiltonian is then

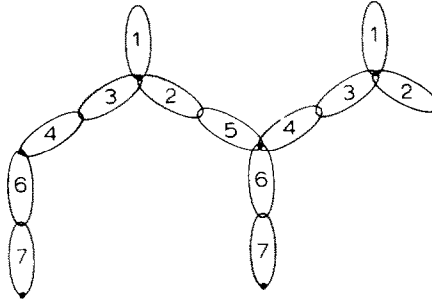


Fig. 3. A part of a surface of a honeycomb lattice with the states labelled. The atoms are represented by solid circles.

$$H = -V \sum_{\langle j, i' \neq i \rangle} |ij\rangle \langle i'j| - V_1 \sum_{\langle i, j' \neq j \rangle} |ij\rangle \langle ij'|, \tag{29}$$

where V is the bonding/antibonding interaction and V_1 leads to the s-p splitting on a single atom [7]. The notation i' means that atom i' is a nearest neighbor of atom i and similarly j' denotes the other state on the same bond j . In the bulk crystal this leads to a 6×6 matrix to be diagonalized at each bulk \mathbf{k} vector and the eigenvalues are easily shown to be (see appendix I):

$$-\frac{1}{2} V_1 \pm [V^2 + \frac{9}{4} V_1^2 \pm V_1 V \epsilon(\mathbf{k})]^{1/2}, \quad V_1 \pm V, \tag{30}$$

where

$$\epsilon^2(\mathbf{k}) = 1 + 4 \cos^2(k_x a) + 4 \cos(k_x a) \cos(\sqrt{3} k_z a) \tag{31}$$

and z is perpendicular to the surface and the near neighbor distance is $2a/\sqrt{3}$. The band edges occur when $E = V_1 \pm V$, $-2V_1 \pm V$, and are shown in fig. 4. The bulk density of states has delta functions at $V_1 \pm V$ which are p bonding/antibonding in character. This is a result of using a simple model Hamiltonian with only near neighbor interactions.

The self-consistent equation for the Green's function g [analogous to eqs. (9) and [19)] can easily be written down. The rows and columns of the matrix are labelled sequentially corresponding to the states 1 to 7 as in fig. 3:

$$g = \begin{pmatrix} E & V_1 & V_1 & 0 & 0 & 0 & 0 \\ V_1 & E & V_1 & V\gamma^* & 0 & 0 & 0 \\ V_1 & V_1 & E & 0 & V\gamma & 0 & 0 \\ 0 & V\gamma & 0 & E & V_1 & V_1 & 0 \\ 0 & 0 & V\gamma^* & V_1 & E & V_1 & 0 \\ 0 & 0 & 0 & V_1 & V_1 & E & V \\ 0 & 0 & 0 & 0 & 0 & V & g^{-1} \end{pmatrix}_{00}^{-1} \tag{32}$$

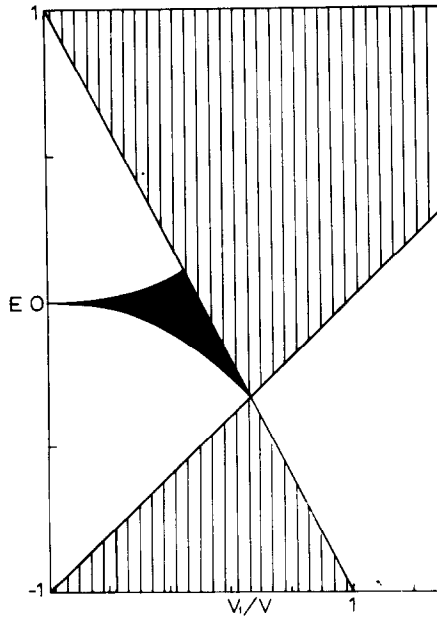


Fig. 4. The bulk energy bands for the honeycomb lattice in the vicinity of the gap are shown by vertical shading as a function of V_1/V and E measured in units of V . The surface band in the gap region is shown by the solid area.

The matrix is now much larger because of the more complex structure. One has to go into the bulk up to orbital 7 until one reaches an orbital “equivalent” to 1. Also

$$\gamma = \exp(ik_x a/2), \tag{33}$$

where a is the distance between atoms on the surface. This equation leads to a quadratic of the same form as eq. (10) for g . Because of the high symmetry of the matrix in eq. (32), it is easy to show (see appendix II) that g obeys eq. (10) with:

$$\begin{aligned} 2\alpha V = & \{V^2 [V^2 - (E^2 - V_1^2)]^2 + [EV^2 - (E + V_1)(E - 2V_1)]^2 \\ & - 4V_1^2 V^2 C^2 [V^2 + (E + V_1)^2]\} \\ & \times \{[V^2 - (E^2 - V_1^2)] [EV^2 - (E + V_1)^2(E - 2V_1)] - 4V_1^2 V^2 C^2 [E + V_1]\}^{-1}, \end{aligned} \tag{34}$$

and

$$C = (\gamma + \gamma^*)/2 = \cos(k_x a/2). \tag{35}$$

From eq. (34) the surface Green function g can be calculated. The quadratic equation (10) always has two solutions. However, the imaginary part of g must be negative if a small imaginary part is added to the energy [condition (13)]. The two

solutions to eq. (10) *must* have imaginary parts with opposite signs and real parts with the same sign and so only one is acceptable by condition (13).

The allowed energy bands are shown in fig. 4. The bulk bands are of a bonding/antibonding character when $V_1/V < 2/3$. A surface Shockley band exists in the gap region in this regime. The lower band limit of the Shockley state occurs at the Γ point ($k_x a = 0$) and is a root of the cubic equation

$$EV^2 = (E^2 - V_1^2)(E + 2V_1), \quad (36)$$

whereas the upper band limit of the Shockley state occurs at the zone boundary (i.e., $k_x a = \pi$) and is a root of:

$$EV^2 = (E - V_1)^2(E + 2V_1). \quad (37)$$

The lower part of the band merges with the bulk bands at the crossover point ($V_1/V = 2/3$) and the upper part merges with the bonding band when $V_1/V = 4/9$. In fig. 5 we show the surface dispersion curves for $V_1/V = 0.4$. The shaded regions are the bulk bands projected onto the surface. The band edges are defined by putting $\cos(\sqrt{3}k_z a) = \pm 1$ in eq. (31), i.e.,

$$\epsilon(k_x) = 1 \pm 2 \cos(k_x a) \quad (38)$$

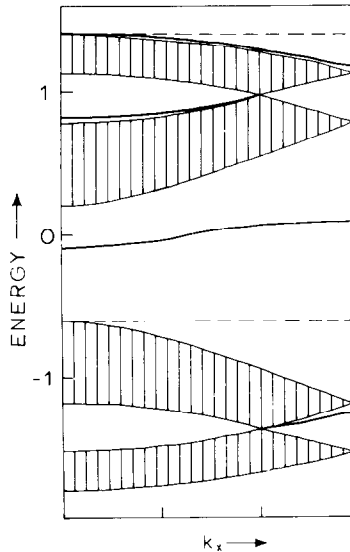


Fig. 5. The surface dispersion for the honeycomb lattice as a function of k_x the surface wave-vector. The energy E is in units of V and the ratio $V_1/V = 0.4$. The zone boundary corresponds to $k_x a = \pi$. The shaded regions are the bulk bands projected onto the surface and the solid lines are localized surface states. The dashed lines are the bulk p bonding/antibonding states.

and then inserting $\epsilon(k_x)$ in eq. (30). It may be seen that at the zone boundary of the surface Brillouin zone (which is a straight line) $\epsilon(k_x) = 1$ and the bulk bands have no width and are located at:

$$-\frac{1}{2}V_1 \pm (\frac{9}{4}V_1^2 + V^2 \pm V_1V)^{1/2}. \tag{39}$$

It is particularly easy to solve for the Green's function at this point. From eqs. (10) and (34) (with $C = 1$) we find that:

$$g = \frac{V^2 - (E^2 - V_1^2)}{EV^2 - (E + V_1)^2(E - 2V_1)}. \tag{40}$$

The other solution to (10) is unacceptable because it does not satisfy condition (13) and also because the condition $Eg \sim 1$ for large E is not obeyed. We see that there are only three surface states at the zone boundary ($k_x a = \pi$) as shown in fig. 5. In fact, this is true for the whole zone although one of these roots "jumps" from the valence band to the conduction band at the point $k_x a = 2\pi/3$. The denominator of (34) allows up to five surface states from the fifth order polynomial in E in the denominator – however, two of these always occur in the unacceptable solution for g in eq. (10).

The local density of states for various surface states is shown in fig. 6 together

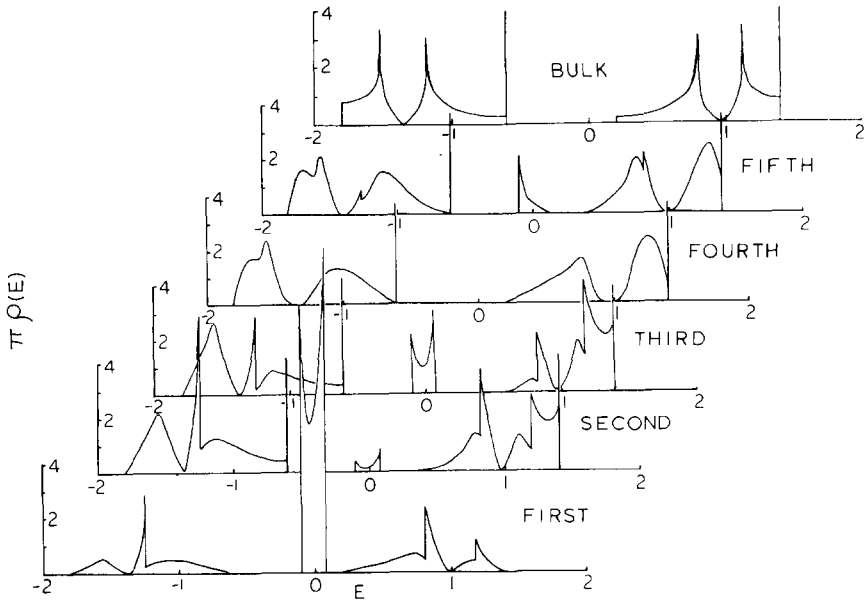


Fig. 6. The surface density of states for the honeycomb lattice for the first five layers in from the surface and for the bulk. The energy E is in units of V and the ratio $V_1/V = 0.4$

with the bulk density of states. The labelling of these states is governed by fig. 3 so that first refers to 1, second to 2 or 3, third to 4 or 5, fourth to 6 and fifth to 7. Notice that the Shockley state is strongest on the surface orbital and absent on atom 6 in the fourth layer, i.e., the atom labelled 6 in fig. 3. The bulk p bonding/antibonding delta functions are absent on the surface orbital. The behavior of the delta functions is discussed in appendix III. Notice also the sharp surface state feature in the center of the valence band – particularly on the back bonds (second and third layers).

5. The 111 surface of the diamond lattice

A calculation for the 111 surface of the diamond lattice using the Hamiltonian (29) proceeds in a very similar way to that for the honeycomb lattice. The labelling of the “sp³” states is shown in fig. 7. The bulk bands are given by (see appendix I):

$$-V_1 \pm [4V_1^2 + V^2 \pm 2V_1 V \epsilon(\mathbf{k})]^{1/2}, \quad V_1 \pm V_2 \text{ (twice)}, \quad (41)$$

where in the conventional cubic axes:

$$\epsilon^2(\mathbf{k}) = 1 + \cos k_x a \cos k_y a + \cos k_y a \cos k_z a + \cos k_z a \cos k_x a, \quad (42)$$

and the nearest neighbor distance is $\sqrt{3}a/8$. The band edges occur when $E = V_1 \pm V$, $-3V_1 \pm V$, and are shown in fig. 8. The bulk density of states has delta functions at $V_1 \pm V$, which are p bonding/antibonding. The self-consistent equation for the Green function g can easily be written down and is similar to eq. (32) except that the matrix is 9×9 rather than 7×7 . Again, a Shockley state appears in the vicinity of the band gap. The lower band edge of this state occurs at the Γ point (the center of the surface Brillouin zone) and is a root of the cubic equation

$$EV^2 = (E - V_1)(E + 2V_1)(E + 3V_1), \quad (43)$$

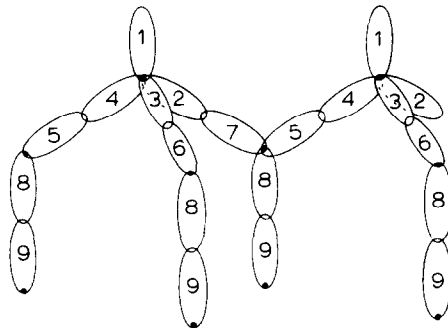


Fig. 7. A part of a 111 surface of the diamond lattice with the states labelled. The atoms are represented by solid circles.

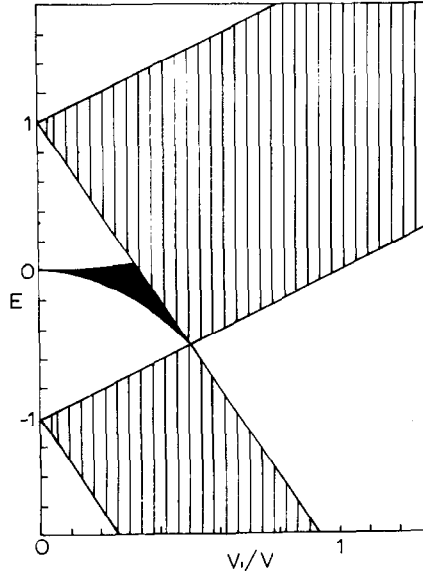


Fig. 8. The bulk energy bands for the diamond lattice are shown by vertical shading as a function of V_1/V and E measured in units of V . The surface band in the gap region is shown by the solid area.

whereas the upper band edge of the Shockley state occurs at the K point (the corner of the hexagonal surface Brillouin zone) and is given by a solution to the equation

$$EV^2 = (E - V_1)^2(E + 3V_1). \tag{44}$$

In fig. 9 it can be seen that there are three surface states at each surface \mathbf{k} vector – and the overall picture is very similar to the honeycomb lattice, especially along the line Γ –K. Note that a constant energy 1.75 eV has been added to the Hamiltonian (29) in order to correspond with ref. [8]. The parameters used are appropriate to bulk Si and/or Ge [8]. The bulk band edges are obtained from eqs. (41) and (42) by rotating to new axes:

$$z' = (x + y + z)/\sqrt{3}, \quad y' = (x - z)/\sqrt{2}, \quad x' = (x - 2y + z)/\sqrt{6}, \tag{45}$$

and letting k_z' take on all values at each k_x', k_y' . The bulk band edges are given by:

$$\epsilon^2(\mathbf{k}) = \pm 1 \pm [1 + 4 \cos^2(k_x', b) + 4 \cos(k_x', a) \cos(\sqrt{3}k_y', a)]^{1/2}, \tag{46}$$

where $b = \sqrt{2}a/4$ and the term under the square root is just the form for the honeycomb lattice (31) as is not surprising from symmetry considerations. The local density of states for various layers are shown in fig. 10 where the labelling is governed by fig. 7 so that first refers to 1; second to 2, 3, or 4; third to 5, 6, or 7;

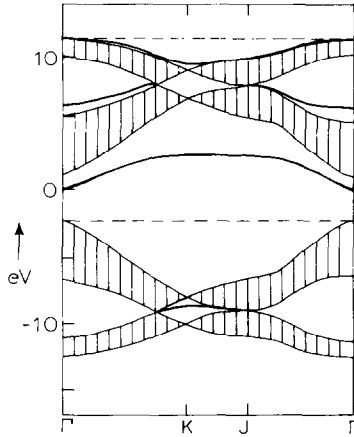


Fig. 9. The surface dispersion for the diamond lattice with $V_1 = 2.5$ eV, $V = 6.75$ eV along symmetry directions in the surface Brillouin zone. This Brillouin zone is a hexagon and K corresponds to a corner and J to the center of an edge. The Γ point is $k = 0$. The shaded regions are the bulk bands projected onto the surface and the solid lines are localized surface states. The dashed lines are the bulk p bonding/antibonding states. Note that a constant energy of 1.75 eV has been added to the spectrum of the Hamiltonian (29).

fourth to 8; fifth to 9. The overall behavior is very similar to the honeycomb lattice with the Shockley state being strongest on the dangling bonds where the p bonding/antibonding states are absent. The Shockley states are absent in the fourth layer from the surface as in the honeycomb lattice.

The models discussed in the previous section have the virtue that various quantities of interest can be obtained algebraically. For example, we obtained expressions for the band edges of the Shockley states as a function of V/V_1 . This could be extended to cases where the surface is reconstructed although of course the algebra rapidly becomes more complicated and much of the virtue of the present model is lost. However, recently Yndurian and Falicov [9] have been able to use the transfer matrix technique to discuss simple surface reconstructions that are restricted to a few layers. In appendix III we discuss another interesting aspect of the model, namely, the weight in the delta functions as a function of the distance from the surface.

6. The Bethe lattice

It is interesting to compare the results of the last two sections with those obtained for a Bethe lattice, using the same Hamiltonian (29). The Bethe lattice is an infinitely branching tree-like structure, the vertices of which we take to be threefold

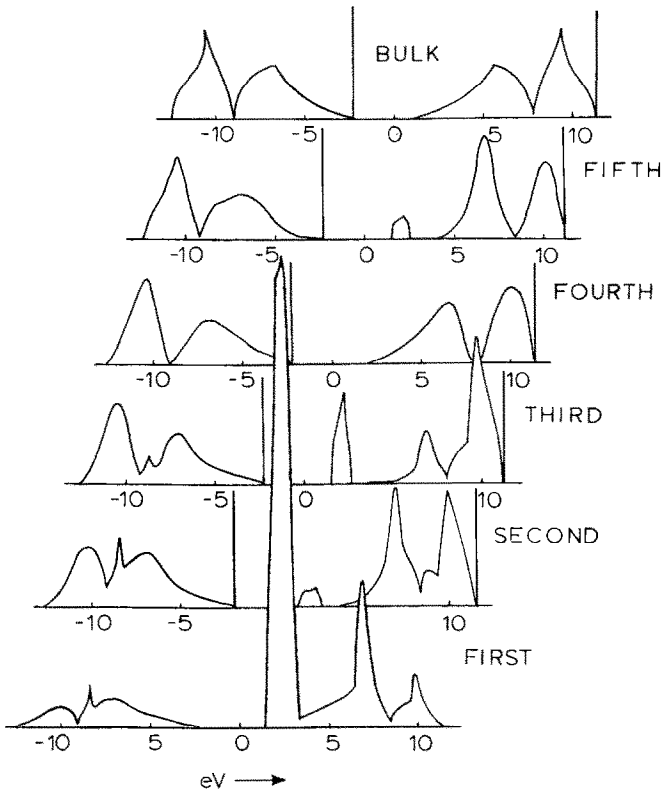


Fig. 10. The surface density of states for the diamond cubic lattice for the first five layers in from the surface and the bulk. The parameters used are the same as fig. 9.

or fourfold coordinated, for comparison with the results for the honeycomb and diamond cubic lattices respectively. Calculations for the Hamiltonian (29) for these bulk Bethe lattices are described elsewhere [7,10]. There are infinitely many ways of forming a “surface” on a Bethe lattice. One of these was described by Nagle et al. [10]. In this case the “surface” had an infinite number of dangling bonds and it was found that the density of states had rather bizarre properties. The density of states was shown to be a series of delta functions which did *not* coalesce to give a continuous spectrum in the thermodynamic limit ($N \rightarrow \infty$).

In the present work we have formed a “dissected” Bethe lattice by cutting a single bond in the center of an infinite Bethe lattice. Thus we form only a single dangling bond. In so much as the surface properties are determined and dominated by a single dangling bond in the previous two sections, this pseudo-lattice should prove helpful. The calculation is very easy to do, and some results have already been given by Gaspard [11] and Goldstein [12].

For the dissected Bethe lattice we may number basis orbitals starting from the

surface, exactly as in previous sections. Again we may relate the Green function g associated with the surface orbital to the Green function g' associated with the bulk (i.e., undissected) system by

$$g = 1/(E - h), \quad (47)$$

where

$$g' = \frac{1}{2} [(E - h + V)^{-1} + (E - h - V)^{-1}]. \quad (48)$$

The bulk Green function g' may be calculated by a variety of methods [7,10], for a general coordination number z , and is given by

$$g' = \{[(E^2 + (z - 2)V_1E + V^2 - (z - 1)V_1^2) \pm [(E^2 + (z - 2)V_1E + V^2 - (z - 1)V_1^2)^2 - 4EV^2(E + (z - 2)V_1)]^{1/2}]\} (2EV^2)^{-1}. \quad (49)$$

The most straightforward way of calculating Green functions associated with other orbitals is to proceed iteratively as follows. The Green function for the n th layer from the surface can be expressed in terms of two fields h , h_n where h represent the infinite interior of the Bethe lattice and h_n describes the rest of the lattice. A recurrence relation can be written relating h_{n+1} and h_n . Starting off with $h_0 = 0$, it is therefore easy to find any required Green function near to the dangling bond. We have refrained from writing down all the algebra as it gets a little messy and the effective field method, as applied to Bethelattices, is by now well known [13]. It is entirely equivalent to either a continued fraction development of the Green function or to the inversion of a matrix as described in previous sections.

The general nature of the solution is as in the previous sections, with a Shockley state at $E = 0$, for $V_1^2/V^2 < (z - 1)^{-1}$. At this critical value the bottom of the conduction band passes through $E = 0$. (For graphs of the bands for various values of V_1/V see Gaspard [11].) The fact that the surface state is fixed at $E = 0$ is not obvious from elementary symmetry arguments but an examination of the perturbation series in (V_1/V) shows that it vanishes so that the state, obviously at $E = 0$ for $V_1 = 0$, must remain there for finite V_1 . (Note that there is only a single state in the Shockley band as we have only a single dnagling bond.) The explicit form of the wavefunction for the Shockley state is as follows. If we give the surface orbital amplitude 1, then an orbital $2n'$ steps away has amplitude $(-V/V_1)^n$ and the intervening ones have *zero* amplitude. Normalizing to unity, we find that the squared amplitude on the surface bond is

$$1 - (z - 1)V_1^2/V^2 \quad (50)$$

which goes to zero at the same point $V_1^2/V^2 = (z - 1)^{-1}$ mentioned above. For $V_1^2/V^2 > (z - 1)^{-1}$, the amplitude of the Shockley state increases exponentially as we go away from the surface and so is not an acceptable solution.

In figs. 11 and 12 we show densities of states calculated for the first five layers by the above methods. In addition to the fall-off of the weighting of the surface

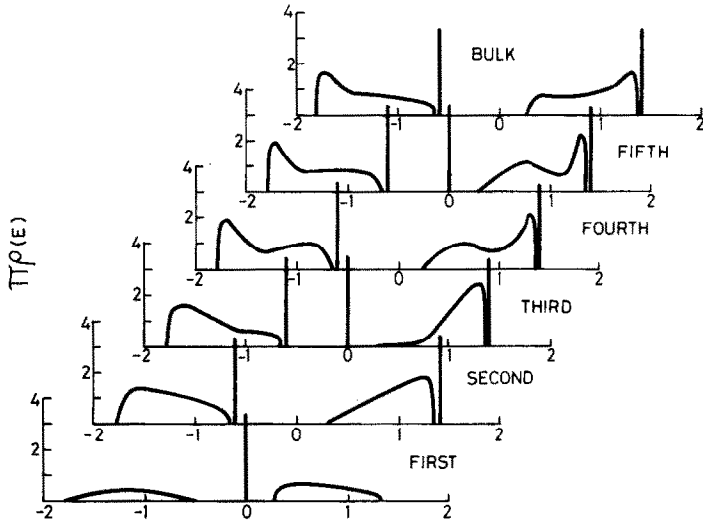


Fig. 11. The density of states for the first five layers in from the dangling bond for a three coordinated Bethe lattice and for the bulk. The units are the same as for fig. 6. The horizontal axis is energy.

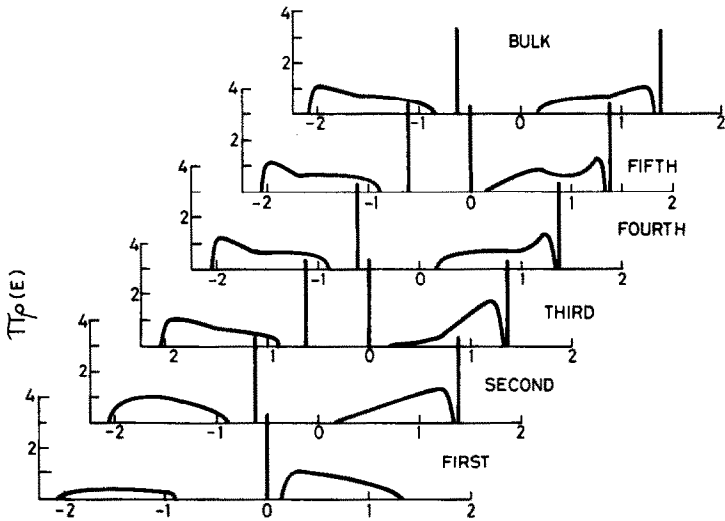


Fig. 12. Same as fig. 11, but for a four-coordinated Bethe lattice. The energy E of the horizontal axis is units of V and the ratio $V_1/V = 0.37$. This density of states is for the same ratio V_1/V as the diamond lattice (fig. 10) although the horizontal scale must be adjusted for a direct comparison.

states, explained above, it is worthy of note that the p-state delta functions do not have the same weight as in the bulk Bethe lattice. For instance, their weight on the first set of basis orbitals from the surface may be extracted analytically from the calculation and is $2/9$ as opposed to $1/4$ for the bulk solution for a Bethe lattice in the case of fourfold coordination. Although this is not a large effect, it is mathematically intriguing, being associated with topological considerations alone (i.e., it does not depend on V_1/V_2). An analysis of the problem is given in appendix III.

Comparisons of these results for $z = 3$ and the honeycomb lattice and for $z = 4$ with the diamond cubic lattice are interesting. In the Bethe lattice, the amplitude of the surface Shockley state vanishes on every other layer. The amplitude of the other layers is largest at the surface and decays exponentially to zero in the bulk with a decay length $\sim [\ln(V_1/V)]^{-1}$. This kind of general behavior can be seen in figs. 6 and 10 for the honeycomb and diamond cubic lattices. The single surface state in the Bethe lattice is broadened into a band and the amplitude is no longer zero on all the even numbered layers. It is small, however, and indeed is rigorously zero on the fourth layer. As this happens for both the honeycomb and diamond cubic lattices, we feel there should be some simple reasoning that would say why, but we have not been able to find it.

There is also a close correspondence in the weights in the delta functions which have zero amplitude on the surface orbital and then increase monotonically to the bulk value with a decay length that depends only on geometry/topology and not on the ratio V_1/V . This is discussed in appendix III.

7. Conclusions

We have tried to show how the use of effective potentials can simplify the algebra of calculating surface states in the tight binding approximation. The method is particularly useful in complex geometries where there is no surface reconstruction. Surface reconstructions, which is always a factor in real systems may be treated as a perturbation at the surface by using equations like (27). The more pedestrian approach of making traditional band structure calculations for finite slabs [2,3] may be preferable if the surface reconstruction is extensive.

We have shown that the weight in the p bonding/antibonding states for "sp^d" Hamiltonians is purely geometrical and independent of the parameters in the Hamiltonian. We have also shown that the behavior of the Shockley states can be largely understood in terms of an appropriate Bethe lattice with a single dangling bond.

We have pointed out that the effective surface potential method is exact for simple tight binding Hamiltonians. As a result the surface Green function can be expressed as a solution of a quadratic equation which depends only on a single parameter α , which depends on the determinants of certain submatrices of the fundamental Hamiltonian (appendix II). The energies of surface states correspond simply to the roots of one of these determinants as described by eq. (A2.4). By com-

parison the effective surface potential method is simpler and easier to apply than the Green function method of KS and the transfer matrix method of FY.

Acknowledgement

We would like to thank F. Yndurain for sending us copies of his work.

Appendix I

In this appendix we discuss a simple way of obtaining the *bulk dispersion relations* for the honeycomb lattice [eqs. (30), (31)] and the diamond lattice [eqs. (41), (42)]. The simple form of these relations results because there is a connection between the eigenvalues of the two-band Hamiltonian:

$$H^{(2)} = -V \sum_{\langle j, i \neq \bar{i} \rangle} |ij\rangle \langle i'j| - V_1 \sum_{\langle i, j' \neq j \rangle} |ij\rangle \langle ij'|, \quad (\text{A1.1})$$

and the one-band Hamiltonian made up of single s states at each site:

$$H^{(1)} = \sum_{\langle i' \neq i \rangle} |i\rangle \langle i'|. \quad (\text{A1.2})$$

In both these Hamiltonians we use the convention on the summations that there is no double counting and for convenience we have set the matrix element in (A1.2) equal to one. Transformations of this kind have been used before by us [7] and others [14].

We will derive the result in general and so we assume that each atom has z nearest neighbors with which it bonds. If the amplitude of a wavefunction of $H^{(2)}$ with energy E at a site labelled i, j (i labels the atom and j the bond) is b_{ij} , then we have (i, i' are at each end of the bond j):

$$Eb_{ij} = -V_1 \sum_{j' \neq j} b_{ij'} - Vb_{i'j}, \quad (\text{A1.3})$$

or

$$(E - V_1)b_{ij} = -V_1 \sum_{j'} b_{ij'} - Vb_{i'j}, \quad (\text{A1.4})$$

similarly

$$(E - V_1)b_{i'j} = -V_1 \sum_{j''} b_{i'j''} - Vb_{ij}. \quad (\text{A1.5})$$

Eliminating $b_{i'j}$:

$$[(E - V_1)^2 - V^2] b_{ij} = -V_1(E - V_1) \sum_{j'} b_{ij'} + V_1 V \sum_{j''} b_{ij''}, \quad (\text{A1.6})$$

and summing over j we obtain:

$$[(E - V_1)^2 - V^2 + zV_1(E - V_1)] \sum_j b_{ij} = V_1 V \sum_{j''} b_{ij''}. \quad (\text{A1.7})$$

If we denote the s like part of wavefunction at site i by:

$$B_i = \sum_j b_{ij},$$

eq. (A1.7) becomes:

$$[(E - V_1)(E + [z - 1]V_1) - V^2] B_i = V_1 V \sum_{i'} B_{i'}, \quad (\text{A1.8})$$

where i' goes over the z neighbors of i . This equation is similar to that for the amplitude A_i of the one-band Hamiltonian at an energy ϵ :

$$\epsilon A_i = \sum_{i'} A_{i'}, \quad (\text{A1.9})$$

and a one-to-one correspondence can be made if we put:

$$\epsilon = [(E - V_1)(E + [z - 1]V_1) - V^2] / V_1 V. \quad (\text{A1.10})$$

i.e.

$$E = V_1(1 - z/2) \pm [V^2 + (zV_1/2)^2 + VV_1\epsilon]^{1/2}. \quad (\text{A1.11})$$

Thus for every eigenstate with energy ϵ of the one-band Hamiltonian we generate two eigenstates of the two-band Hamiltonian via eq. (A1.11).

This procedure generates all eigenvalues except for those that are entirely p-like on each atom. Instead of just two states/atom, we should generate z states/atom; the remaining $(z - 2)$ states are equally divided between p bonding/antibonding states (i.e., for the linear chain discussed in section 2, there are no such states, for the honeycomb $\frac{1}{2}$ state/atom and for the diamond lattice 1 state/atom, that is, the weight in the delta functions becomes relatively more important as z increases).

A further simplification can be achieved by noting that the Bravais lattices for the honeycomb and diamond lattices are the triangular net and the face centered cubic lattice, respectively. Both the honeycomb and diamond lattices are bichromatic. Each atom is surrounded by neighbors in the other sublattice -- the sublattices being the appropriate Bravais lattice. Thus, by "squaring" the one-band Hamiltonian (A1.2) -- a one-band Hamiltonian for the Bravais lattice is produced (apart from a diagonal term z). If the eigenvalues of the one-band Hamiltonian (A1.2) for the Bravais lattice are ϵ_B , then

$$\epsilon^2 = \epsilon_B + z. \tag{A1.12}$$

But the ϵ_B are simply given by:

$$\epsilon_B = \sum_{\delta} \exp(i\mathbf{k} \cdot \delta) \tag{A1.13}$$

for \mathbf{k} vectors going over the first Brillouin zone of the Bravais lattice. If the nearest neighbor distance is d for the Bravais lattice, then (A1.13) becomes: linear chain,

$$\epsilon_B(\mathbf{k}) = 2 \cos(kd);$$

triangular net,

$$\epsilon_B(\mathbf{k}) = 2 \cos(k_x d) + 4 \cos(k_x d/2) \cos(\sqrt{3}k_z d/2); \tag{A1.14}$$

face centered cubic,

$$\epsilon_B(\mathbf{k}) = 4 [\cos(k_x d/\sqrt{2}) \cos(k_y d/\sqrt{2}) + \cos(k_y d/\sqrt{2}) \cos(k_z d/\sqrt{2}) + \cos(k_z d/\sqrt{2}) \cos(k_x d/\sqrt{2})].$$

Our results may be summed up by giving the eigenvalues and their degeneracies:

$$V_1(1-z/2) \pm \{V^2 + (zV_1/2)^2 \pm VV_1[z + \epsilon_B(\mathbf{k})]^{1/2}\}^{1/2}, [1/2 \text{ state/atom}];$$

$$V_1 \pm V, \tag{A1.15} \quad [(z-2)/2 \text{ states/atom}].$$

Appendix II

The surface Green function depends solely on the parameter α [see eq. (12)], and so it is useful to derive a simple expression for it. We shall use the honeycomb lattice as an example for illustration. Eq. (32) can be written as

$$g = \begin{bmatrix} E & V_1 & V_1 & 0 & 0 & 0 & 0 \\ V_1 & E & V_1 & V\gamma^* & 0 & 0 & 0 \\ V_1 & V_1 & E & 0 & V\gamma & 0 & 0 \\ 0 & V\gamma & 0 & E & V_1 & V_1 & 0 \\ 0 & 0 & V\gamma^* & V_1 & E & V_1 & 0 \\ 0 & 0 & 0 & V_1 & V_1 & E & V \\ 0 & 0 & 0 & 0 & 0 & V & g^{-1} \end{bmatrix}^{-1} \tag{A2.1}$$

After some algebraic manipulation, eq. (A2.1) becomes

$$g = (D_5 - V^2 D_4 g) / (D_6 - V^2 D_5 g), \tag{A2.2}$$

which can be expressed as a quadratic equation for g . By comparing it with eq. (10), one obtains

$$\alpha = (D_6 + V^2 D_4)/(2VD_5). \quad (\text{A2.3})$$

In eqs. (A2.2) and (A2.3), D_4 , D_5 and D_6 are the determinants of the 4×4 , 5×5 and 6×6 matrices circled by the dash-lines. Eq. (34) can be reproduced after expanding these determinants. The energies of the surface states can be obtained by solving

$$D_5 = 0. \quad (\text{A2.4})$$

Similar expressions can be derived for the diamond lattice.

Appendix III

In this appendix, we consider the question of the weights in the p bonding/anti-bonding δ functions. These states are *pure* bonding/antibonding and p-like even in the presence of a surface. The p-like character means that the sum of the z amplitudes associated with each *atom* is zero. The bonding/antibonding character means that the amplitudes of the wavefunctions on a *bond* are the same/opposite. It is clear that there must be the same weight in both the bonding and antibonding δ functions as one can be obtained from the other by changing the sign of half the amplitudes. There are never any geometrical constraints preventing this. The weight in the p bonding states in the *bulk* can be determined by the following argument. There are z states/atom and to make the character p-like we must impose 1 constraint/atom and to make it bonding, another $z/2$ constraints/atom. A little thought will convince the reader that these constraints are independent. Thus we have $z - 1 - z/2 = z/2 - 1$ ways of making p bonding states/atom, i.e., $(z - 2)/2z$ per orbital. That is, $1/6$ of the weight in the honeycomb lattice and $1/4$ of the weight in the diamond cubic lattice is in the p bonding states.

This argument has to be modified in the presence of a surface when all lattice sites are no longer equivalent. There will be extra constraints associated with the dangling bonds. Indeed, the only way the state can be pure bonding is if there is *zero amplitude* on the dangling bond itself. This can be seen in figs. 6, 10–12. We write the weight W_i on the i th orbital as

$$W_i = (z - 2)/2z(1 - D_i) \quad (\text{A3.1})$$

where the deficiency D_i will go to zero as we go into the bulk. There is effectively an extra $1/2$ constraint/dangling bond so that

$$\frac{1}{2} = (z - 2)/2z \sum_i D_i, \quad \text{i.e.,} \quad z/(z - 2) = \sum_i D_i, \quad (\text{A3.2})$$

where the summation goes over all orbitals that can be associated with each dangling

bond. In the dissected Bethe lattice this is over the entire lattice as there is only a single dangling bond. In the honeycomb lattice (see fig. 3) orbitals 2 (which is equivalent to 3) gets weight 2, orbital 5 also gets weight 2 and orbitals 6 and 7 each get weight 1. It is clear because of the bonding character that the weights of 2 and 5 will be the same as will the weights of 6 and 7.

These p bonding states define a subspace of the Hamiltonian (29) that is independent of V_1 and V . Therefore, the weight in these states follows from purely geometrical/topological considerations. This is an unusual situation and may be exploited to simplify the calculation of the D_i . Because the p bonding states are degenerate, there are many possible ways of describing them – one of the simplest is in terms of rings and chains. If a closed ring of bonds or an open ring (chain) of bonds is defined, then a p bonding wavefunction has finite amplitude only along the chain and the wavefunction looks like ... ++ -- ++ -- ++ ... where there is a plus and a minus (and also a zero) associated with each atom and the state is clearly bonding. Of course the D_i can be found directly from the algebra developed in this paper but considerable simplification results if we only work within the subspace of the p bonding states and we illustrate this with the honeycomb lattice. In this case, we have $1/2$ p bonding state/atom which just happens to be the same as the number of hexagons in the lattice. We therefore have immediately a complete set of states within the subspace using the p bonding states ++ -- ++ -- ++ -- on each of the hexagons. Those are clearly linearly independent although they are not orthogonal. The problem then is to orthogonalize these states and then find the weights on the various hexagons and then on the appropriate bond. We define an overlap matrix

$$0 = \sum_i |i\rangle\langle i| - \frac{1}{6} \sum_{i,\delta} |i\rangle\langle i + \delta|, \quad (\text{A3.3})$$

where the normalized states $|i\rangle$ are the ring states on the hexagons and the overlap integral between adjacent hexagons is $-1/6$. The sum over i goes over the centers of the hexagons which defines the dual lattice of the honeycomb which is triangular net. The matrix (A3.3) can be diagonalized using the methods described in this paper applied to the triangular net. If the eigenvectors are $|E\rangle$, then we need to know quantities like

$$\sum_E |\langle i|E\rangle|^2. \quad (\text{A3.4})$$

The result for the D_i [eq. (A3.2)] can be expressed as an integral over the surface Brillouin zone which can be evaluated analytically and is – for the back bonds (orbitals 2, 3, 4, 5 in fig. 3), $D_i = 2 - 3\sqrt{3}/\pi = 0.346$ and for the next bonds in (orbitals 6, 7 in fig. 3), $D_i = 10 - 18\sqrt{3}/\pi = 0.076$ so that the sum rule (A2.2) becomes

$$3 = 1 + 4(0.346) + 2(0.076) + \dots \quad (\text{A3.5})$$

It can be seen the D_i tend rapidly to zero. The numbers found above agree closely

with the numerical calculations previously described where a small imaginary part was added to the energy to broaden the δ functions into lorentzians.

It is illuminating to also calculate the D_i for the dissected Bethe lattice. The simplest way to obtain these is to consider only the *bonding* states (both *s* and *p*-like atomically) and also to treat the single broken bond as a point defect in an otherwise infinite Bethe lattice. It is then possible to show that the deficiencies D_i [eq. (A3.1)] in the amplitude of the *p* bonding state decrease by a factor $1/(z-1)^2$ for each additional generation on the tree. We know that this state is completely absent on the dangling bond itself and so the deficiency here must be 1 and so on subsequent layers, it is $(z-1)^{-2}$, $(z-1)^{-4}$ etc. Thus, for the $z=3$ case, we have $D_i = 0.25$ for the back bond (compared with 0.346 in the honeycomb) and $D_i = 0.0625$ on the next layer (compared with 0.076 in the honeycomb). The sum rule (A3.2) becomes:

$$3 = 1 + 4(0.025) + 8(0.0625) + \dots \quad (\text{A3.6})$$

Notice first that the factors preceding the brackets in (A3.6) *increase* as we go into the bulk for the Bethe lattice whereas they are always 2 or 4 for the honeycomb lattice. Therefore, because we have the same sum rule in both cases, the D_i must decay *more rapidly* to zero in the Bethe lattice for which the decay length is $\sim [\ln(z-1)]^{-1}$ layers. We see that this is a very small length so that the weight in the *p* bonding state rapidly attains its bulk value as we move in from the surface. Secondly, it happens even more rapidly for larger z . For a general z , the sum rule (A3.2) becomes

$$\frac{z}{z-2} = 1 + 2(z-1) \frac{1}{(z-1)^2} + 2(z-1)^2 \frac{1}{(z-1)^4} + \dots \quad (\text{A3.7})$$

Thus for $z=4$, we have $D_i = 0.111$ for the back bonds and $D_i = 0.012$ for the next layer. We have not made an analytic calculation of these numbers for the diamond cubic lattice – however, the numerical calculations give numbers just a little larger than for the $z=4$ Bethe lattice as we would expect.

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