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## Electronic structure based on the local atomic environment for tight-binding bands

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**Abstract.** Some new methods are presented for calculating the density of states  $n(E)$  and other aspects of electronic structure in a tight-binding band, without use of Bloch's theorem or the band structure  $E(k)$ . The methods are therefore applicable to calculating the local density of states at surfaces, impurities etc and relate the electronic structure to the local atomic environment. They depend on developing the Green function as an infinite continued fraction. There is no difficulty in obtaining  $n(E)$  in a few minutes computing time correct to the first 50 moments for an s band and 10 moments for d bands. The present paper discusses the methods and ideas, with specific applications to follow.

### 1. Electronic structure and local environment

The present work concerns calculating the electronic structure of a solid when this can be represented in a tight-binding formalism (or the lattice vibrations in a force constant model). The method does not involve the use of Bloch's theorem or the band structure  $E(k)$  in any way. Instead, the electronic structure at one atomic site is related to the local environment of near neighbouring atoms. The method can therefore be applied to the electronic structure at a surface, with or without an adsorbed atom, or at an impurity in the bulk. Even for the bulk properties of a perfect crystal the method may have some advantages. Firstly the density of states  $n(E)$  is obtained as an analytic expression without sampling  $E(k)$ . Secondly the electronic structure is related to the chemical bonding of an atom to its near neighbours, and the variation of the bond order through the band can be obtained for example. The transport properties of solids are most naturally discussed in terms of  $E(k)$  with the machinery of Fermi surfaces, effective masses, electrons and holes. But in other situations the wavevector  $k$  may be irrelevant, a given property depending perhaps on just the density of states. Our method will be used to discuss how large a cluster of similar atoms is required before the central atom behaves the same way as in bulk material. It is equally applicable to a finite cluster with a small number of atoms, as to an infinite solid. It seems the method might also be used for disordered alloys and random structures. Specific applications currently under study in Cambridge include the electronic structure of transition metals at a surface, the relative energies of different phases for transition metals, in particular some complex alloy phases, the atomic moments in magnetic alloys, and lattice vibrations at surfaces.

In order to discuss electronic structure when perfect periodicity is lacking, Friedel introduced the 'local density of states' (Friedel 1954, Kittel 1963, p 339, Heine and

Weaire 1970, p 433)

$$\begin{aligned} n(E, r) &= \sum_n |\psi_n(r)|^2 \delta(E - E_n) \\ &= -\pi^{-1} \text{Im } G(r, r, E + i\epsilon) \end{aligned}$$

where

$$G(r, r', E) = \langle r | (E - H)^{-1} | r' \rangle \quad (1.1)$$

and the other properties can also be expressed in terms of the Green function  $G$  or resolvent  $(E - H)^{-1}$ . Analogous expressions can be written down relevant to a tight-binding hamiltonian  $H$ . In order to explain our ideas and discuss their relation to previous work, we shall write down our method for the present in its simplest possible form. We shall assume that the electronic structure arises from a set of similar  $s$  states  $|j\rangle$  centred on the atomic sites  $j$ . The hamiltonian  $H$  represents a constant interaction energy  $h$  between nearest neighbour atoms (only), and the zero of energy has been chosen so that the diagonal matrix elements of  $H$  are zero. Clearly for realistic calculations the method has to be generalized to several states on each atom, not  $s$  states, to more distant overlaps, to different types of atoms with different diagonal energies: all this is straightforward and has been discussed by F Cyrot and co-workers in their study of the same problem (see below). For transition metals it is also possible to include the hybridization of the local  $d$  states with a free-electron  $sp$  band (Cyrot-Lackmann *et al* 1970, Haydock 1972). We also assume the basis states  $|j\rangle$  have been orthogonalized or that  $H$  is a pseudo-hamiltonian where the overlap between the states  $|j\rangle$  does not arise (Anderson 1958, Pettifor 1969). With these simplifications, the analogue of (1.1) becomes

$$n_0(E) = -\pi^{-1} \lim_{\epsilon \rightarrow 0} \text{Im } G_{00}(E + i\epsilon) \quad (1.2a)$$

where

$$G_{ij}(E) = \langle i | (E - H)^{-1} | j \rangle \quad (1.2b)$$

and we have labelled as atom zero the particular atom we are interested in. For a crystal with periodic boundary conditions,  $n_j(E)$  is of course the same on all atoms  $j$  and equal to the total density of states  $n(E)$  normalized to one per atom: in such cases we shall drop the suffix 0 on  $n(E)$  and  $G$ . Our recursion method (§3) and the simpler selfconsistent method (§2) both evaluate  $n(E)$  by a continued fraction expression for (1.2b).

Other authors have developed the 'method of moments' for solving the same problem, that is producing an approximation to  $n(E)$  without calculating the eigenvalues  $E_n$  (Cyrot-Lackmann 1967, 1968, 1970, Cyrot-Lackmann and Ducastelle 1970, 1971a, b, Allan and Lengart 1970, Gerl 1970). Their methods use the moments  $\mu_r$  of the density of states distribution  $n(E)$ ;

$$\begin{aligned} \mu_r &= \int_{-\infty}^{\infty} E^r n(E) dE \\ &= \sum_n E_n^r \\ &= \text{Tr} \{H^r\} = \sum_j \langle j | H^r | j \rangle. \end{aligned} \quad (1.3a)$$

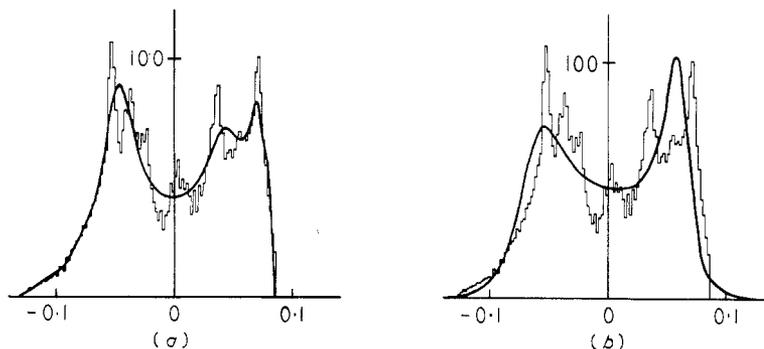
The corresponding result for the  $r$ th moment of the local density of states on atom 0 is

$$\begin{aligned}\mu_{0r} &= \int_{-\infty}^{\infty} E^r n_0(E) dE \\ &= \langle 0 | H^r | 0 \rangle\end{aligned}\quad (1.3b)$$

$$= \sum_{abc\dots k} H_{0a} H_{ab} H_{bc} \dots H_{k0} \quad (1.4)$$

where the last step follows by simple matrix multiplication. Since the matrix elements  $H_{ij}$  are zero except for nearest neighbour overlap, the only nonzero contributions to (1.4) come from 'chains' of neighbouring atoms  $0abc\dots k0$ . These must be closed chains starting and finishing at atom zero. Thus  $\mu_r$  or  $\mu_{0r}$  can be calculated by counting the number of such chains of length  $r$ . The moment method basically consists of obtaining all moments up to some maximum order  $m$ , and then fitting a suitable function  $n(E)$  to these by one of several means.

In practice the moment method works well if one has moments up to a high order, but these become tedious to evaluate beyond about the tenth, particularly when for d bands one has to sum over all five d states at every intermediate atom along each chain. By contrast with our recursion method (§3) we obtain formulae for the densities of states which reproduce the first 50 moments exactly for s bands and the first 10 moments for d bands, in about 3 minutes of computing time, although in practice we do not evaluate or use the moments themselves (figure 1). The moment method is less satis-



**Figure 1.** Density of states for d band in face centred cubic structure. Histogram—exact results from sampling  $E(k)$  after Pettifor (1970): (a) full line, recursion method correct to tenth moment; (b) broken line, selfconsistent method correct to fourth order.

factory if one only has a small number of moments, for as is well known, there is a very wide diversity of functions which have, say, the first four moments identically the same. However this fact itself presents a paradox which provided the original stimulus to the present work. A variety of experimental evidence and theoretical ideas (see for example Heine and Weaire 1970, p 436) suggests that  $n_0(E)$  on one atom on the whole does not depend strongly on the atomic environment beyond first or second nearest neighbours. It should therefore not be necessary to consider long chains to distant neighbours. One tentatively concludes that the largest contribution to the high moments comes from chains that wind around the central atom in multiple repetitions of simple loops (figure 2). We shall return to this question in §2 and in future work on finite clusters.

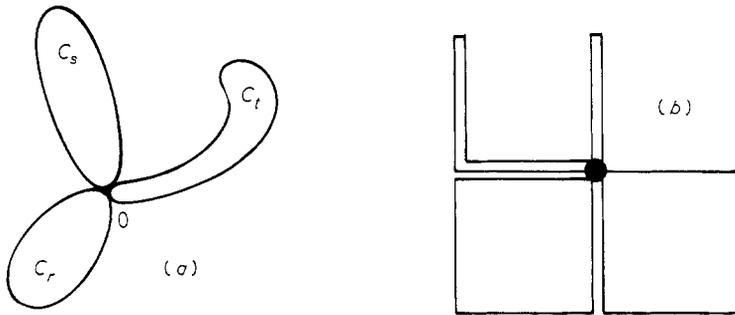


Figure 2. Multiple repetition of small irreducible chains around a central atom. (a) the reducible chain  $C_r C_s C_t$  is generated by

$$E \left[ 1 - \frac{C_r}{E^r} - \frac{C_s}{E^s} - \frac{C_t}{E^t} \right]$$

(b) A reducible 14th order chain consisting of four irreducible subchains.

## 2. The selfconsistent method, the cluster method and other ideas

The present section serves several purposes. Our best method, the recursion method, is described in §3 which is logically selfcontained and may be read without reference to the present section. However some aspects of it must appear rather arbitrary without a certain background of ideas which we have gleaned from the work of others mostly in quite different contexts including lattice vibrations, the Ising model, disordered materials, Padé approximants, and the classical moment problem. These ideas we present briefly here. They have led us to explore various methods of calculating  $G_{00}$  (1.2) and we include an outline of the two best: the selfconsistent method and the cluster method. Indeed there is no finite set of particular methods but rather a series of ideas which can be combined in various ways. They are sufficiently inviting that others will feel bound to explore them if we do not publish our experience with them. Although on the whole we feel now that the recursion method (§3) supersedes the rest, the selfconsistent method gave results (figure 1) which we found very gratifying at the time and the cluster method is probably better. In some ways the methods of this section are somewhat simpler than the recursion method, certainly close to physical intuition in concept, and they may find application on that count.

The resolvent operator in (1.2) may be expanded as a power series in  $H/E$  involving the moments:

$$\begin{aligned} G_{00}(E) &= E^{-1} \langle 0 | 1 + \sum_m H^m / E^m | 0 \rangle \\ &= E^{-1} \left( 1 + \sum_m \frac{\mu_{0,m}}{E^m} \right). \end{aligned} \quad (2.1)$$

With the interpretation (1.4) of the moments, we see that  $G_{00}(E)$  is a sum over all chains from atom zero. Alternatively  $G_{00}(E)$  can be written in terms of the eigenstates  $|n\rangle$  of  $H$ ,

$$G_{00}(E) = \langle 0 | \sum_n \frac{|n\rangle \langle n|}{E - E_n} | 0 \rangle \quad (2.2)$$

which shows that  $G_{00}(E)$  is analytic in the complex  $E$  plane except for poles at the eigenvalues on the real axis. For an infinite solid the line of poles becomes a cut, which is of finite extent around  $E = 0$  since we are considering a single tight-binding band. Thus (2.1) converges as a power series in  $E^{-1}$  around the point  $E = \infty$  with circle of convergence reaching  $E_{\max}$ , the maximum  $|E_n|$ . The series (2.1) diverges outside this region, in particular along the cut where we would wish to evaluate it in (1.2). The problem is to develop a systematic approximation to  $G_{00}(E)$  which is a Herglotz function (Shohat and Tamarkin 1943, Akhiezer 1965) in the entire complex  $E$  plane. A Herglotz function  $f(E)$  has

$$\operatorname{Im} f > 0 \text{ for } \operatorname{Im} E < 0 \quad \operatorname{Im} f < 0 \text{ for } \operatorname{Im} E > 0 \quad (2.3)$$

which guarantees a positive definite density of states and no poles (or cut) except on the real axis, so that it corresponds to some hamiltonian (Akhiezer 1965).

The first step is to apply a 'linked cluster' type of summation to (2.1):

$$G_{00}(E) = \frac{1}{E - \sum_m \bar{\mu}_{0m}/E^{m-1}}. \quad (2.4)$$

Here  $\bar{\mu}_{0m}$  is the sum of all 'irreducible' chains of type (1.4), that is those which do not return to atom 0 at any of the intermediate steps  $abc \dots k$  (see figure 2).

Truncating (2.4) at some finite order  $n$  does not yield a Herglotz function. For example we have for the simple cubic structure with overlap integral  $h$

$$G_{00}(E) = \frac{1}{E - 6h^2/E - 54h^4/E^3} \quad (2.5)$$

truncated at the fourth order. This can be resolved into partial fractions when it is seen to have two poles on the real axis and two at complex  $E$ . However a continued fraction

$$G_{00}(E) = \frac{1}{E - a_1 - \frac{b_1}{E - a_2 - \frac{b_2}{E - \dots}}} \quad (2.6)$$

is a Herglotz function if all the  $b_n$  are positive, even when truncated at any finite order (Shohat and Tamarkin 1943). Unfortunately the renormalized perturbation expansion for  $G(E)$  (Economou and Cohen 1971), while rather similar to (2.6), does not seem to share this property. Only for a one dimensional chain, Economou's expression reduces to the form (2.6) and an exact solution for  $G(E)$  is obtained, as recognized earlier by Anderson and others.

One way of obtaining sensible results from (2.5) is to turn it into a continued fraction:

$$\begin{aligned} E - \frac{6h^2}{E} - \frac{54h^4}{E^3} &= E - \frac{6h^2}{E(1 + 9h^2/E^2)^{-1}} \\ &= E - \frac{6h^2}{E - \frac{9h^2}{E} + O(E^{-2})}. \end{aligned} \quad (2.7)$$

We now drop the higher order terms in (2.7), which is equivalent to supplying some higher order terms in (2.5) in place of the truncated exact ones. (2.7) gives a density of states consisting of four delta functions with the correct moments up to fourth order. The

procedure can be applied to (2.4) truncated at any given order and kept exact to that order.

An alternative approach is to write down a 'Dyson' type of selfconsistent equation for  $G$ . A simple type of chain is shown in figure 3*a*, involving a step out to atom 1, then

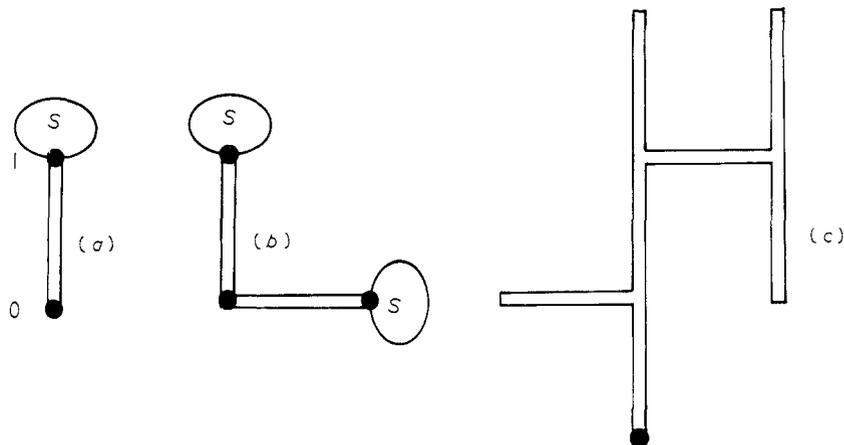


Figure 3. (a) An irreducible chain from atom zero. (b) Excursions from atom 1, avoiding atom zero. (c) A 'tree' included in (2.8).

some unspecified path (avoiding atom zero) returning to atom 1, and finally back to atom zero. Let  $S$  be the sum of all the intermediate excursions from atom 1. Using again the decomposition of reducible chains as in (2.4), (2.5), we can write approximately

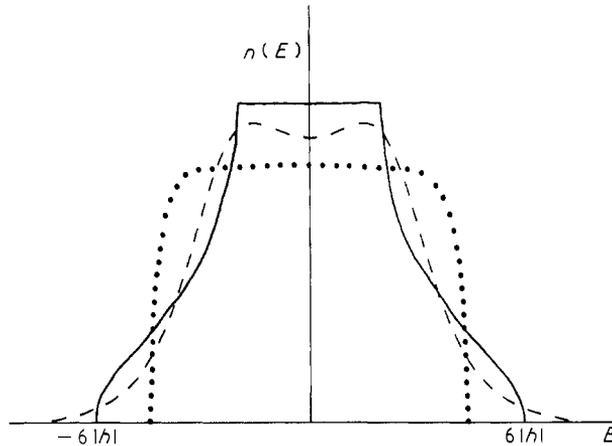
$$G_{00}(E) = \frac{1}{E - \frac{6h^2}{E} S} \quad (2.8a)$$

which includes all chains of the type shown in figure 3*a*, together with all 'reducible' chains consisting of a succession of such irreducible subchains. Figure 3*b* shows that  $S$  can itself be written in similar form

$$S(E) = \frac{1}{1 - \frac{5h^2}{E^2} S(E)} \quad (2.8b)$$

yielding a selfconsistent equation for  $S$  for substitution in (2.8). In general in (2.8*a*) the coefficient 6 would be replaced by  $z$ , the number of nearest neighbours, whereas  $z - 1$  appears in (2.8*b*) because a step back to atom zero would give a reducible chain which is already counted in (2.8*a*). The approximation (2.8) for  $G_{00}(E)$  includes all tree-like chains (figure 3*c*): actually there is some double counting of long chains which in our prescription can curl around back through atom zero but the error starts at quite a high order. The results are shown in figure 4. No such looping back can occur for the one dimensional problem, where squares and other shaped chains are also absent, so that (2.8) gives the density of states exactly (Anderson *et al* 1970).

The expression (2.8) for  $G$  can be evaluated in two different ways. The obvious one is



**Figure 4.** Density of states for simple cubic  $s$  band by selfconsistent method. Dotted line, correct to second order from (2.8); broken line, correct to fourth order from (2.12); full line, exact results calculated from the band structure.

to solve the quadratic equation (2.8b),

$$E^{-1}S(E) = \frac{E - \{E^2 - 4(z-1)h^2\}^{1/2}}{2(z-1)h^2} \quad (2.9)$$

where we have written down the general solution for  $z$  nearest neighbours. The density of states is zero outside the range of the cut

$$|E| \leq 2(z-1)^{1/2}h \quad (2.10)$$

produced by the square root. Alternatively one can substitute the whole expression (2.8b) in place of the  $S(E)$  in the denominator of (2.8b), and so on repeatedly, thus generating an infinite continued fraction. Conversely we note that an infinite continued fraction (2.6) with constant coefficients gives a rather featureless density of states (figure 4) having no interior van Hove singularities but with the correct behaviour

$$n(E) \propto (E - E_{\max \min})^{1/2} \quad (2.11)$$

at the band edges. (The case  $z = 2$  yields a special cancellation between (2.8a) and (2.8b) resulting in the inverse square root singularity in  $n(E)$  appropriate to one dimensional bands.)

It should be pointed out that (2.8) can be given a physical interpretation. If in (2.8a) we set  $S = 1$ , we have an exact solution to the finite cluster of seven atoms: for the simple cubic lattice none of the six neighbours are nearest neighbours to one another and so no triangular etc chains are possible. The factor  $S$  in (2.8a) represents the interaction of the neighbour with the surrounding solid, which can of course be varied. In our case we know that the band extends over the range  $|E| \leq 6h$ : for  $s$  states on any lattice the most bonding state always has energy  $-zh$ . We could therefore use this fact to improve our results by employing the form (2.9) for  $S$  but adjusting the coefficient in (2.9) to give the correct bandwidth instead of (2.10).

We can now put these various ideas together to obtain what we call the selfconsistent

method. Let us extend (2.8) to the next order, still for the simple cubic lattice.

$$G_{00}(E) = \frac{1}{E - 6h^2g_1 - 24h^4g_1^2g_2} \quad (2.12a)$$

$$g_1(E) = \frac{1}{E - 5h^2g_1 - 16h^4g_1^2g_2} \quad (2.12b)$$

$$g_2(E) = \frac{1}{E - 4h^2g_1 - 10h^4g_1^2g_2}. \quad (2.12c)$$

Here we have written  $g(E)$  for  $E^{-1}S(E)$ , the partial propagators, and distinguished between  $g_1$  and  $g_2$  according to whether excursions to  $z - 1$  or  $z - 2$  nearest neighbours are allowed. For example from atom 3 in figure 5, we must avoid atom zero to keep the chain irreducible, and we must not make an excursion via atom 2 because that gives a chain which would already have been classified and counted as an excursion from atom 2. In (2.12a) the coefficient 24 derives from the number of square chains, all other fourth order chains being 'trees' and thus generated by  $g_1$  in the second order term as in (2.8).

Solving (2.12b), (2.12c) as quartic equations for  $g_1, g_2$  does not yield Herglotz functions for similar reasons as for (2.5): it only works for quadratic equations as in (2.8b), (2.9). We therefore must turn our equations into a continued fraction as in (2.7). Moreover we do not just wish to keep accuracy to fourth order in the final result for  $G_{00}$ : almost anything we did with the equations would do that. If we had some extension of (2.8b) correct to fourth order, then we would be keeping that accuracy at every iteration of that equation, that is we would be keeping fourth order accuracy in some sense at every level of the infinite continued fraction. Let us take the latter point of view as our guide. The algebra proceeds by noting that  $g_1, g_2$  are of order  $E^{-1}$  as  $E \rightarrow \infty$ , and pulling out a factor of  $E^{-1}$  at every stage. First  $g_1$  is abbreviated to  $(E - P_1)^{-1}$  where  $P_1$  is a polynomial in  $g_1, g_2$ . We have

$$Eg_1 = 1 + P_1g_1 \quad (2.13)$$

with a similar form for  $g_2$ , and use this to substitute symmetrically for one factor of  $g$  or  $g_2$  in each term of  $G$ , obtaining

$$G_{00}(E) = \frac{1}{E - bE^{-1}(1 + Q)}. \quad (2.14)$$

Here  $Q$  is a polynomial in  $g_1, g_2$  starting with the first power, the constant term having been taken out as shown. (2.14) becomes

$$G_{00}(E) = \frac{1}{E - \frac{b}{E(1 + Q)^{-1}}}. \quad (2.15)$$

In the last line  $(1 + Q)^{-1}$  can be expanded to any accuracy desired, our procedure being quite general. The first term in  $E$  is retained, and the rest of the series  $-EQ + EQ^2 - \dots$  is turned into a new polynomial in  $g_1, g_2$  by taking one factor of  $g_1$  or  $g_2$  symmetrically from each term and using (2.13). We recover an expression of the same form as the denominator of (2.12a), which completes one cycle of turning  $G_{00}(E)$  into a continued fraction. The algebra of this process has been programmed into the computer and after about 30 stages we find that the coefficients  $a_n, b_n$  of the continued fraction have settled down to effectively constant values. The stages beyond that are equivalent to the solution of a quadratic equation, as discussed in connection with (2.8b), (2.9), which can

therefore be inserted at that point. There appears to be no guarantee that the coefficients  $b_n$  all turn out positive, as is necessary for a positive definite density of states, but this has in fact been so in all the cases we have calculated.

The results for the s band on a simple cubic lattice are shown in figure 4, derived from (2.12) and kept correct to fourth order at every step. There is a substantial improvement over the second order results (figure 4). Indeed it is interesting that the very simple chains of figure 5 give already such good results. For d bands it is necessary to sum over all five d states at atom zero in (1.2) and at all atoms  $a b c \dots$  on the chain in (1.4), the exact mechanics of which will be discussed elsewhere (Haydock to be published). The results have already been shown in figure 1.

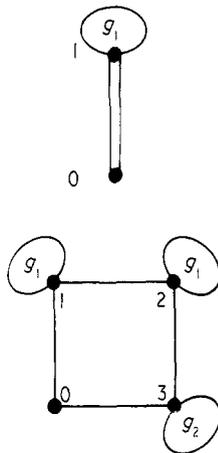


Figure 5. Irreducible chains contributing to (2.12).

Finally we indicate a further improvement on the selfconsistent method which we call the cluster method. As before, the problem is to obtain a Herglotz function. In this method we note that  $G_{00}(E)$  must turn out Herglotz if we write it down *exactly* for a real system, even though it does not have the manifestly Herglotz form of a continued fraction. Let us consider the two dimensional square lattice and pick out a cluster of 9 atoms  $0ab \dots gh$

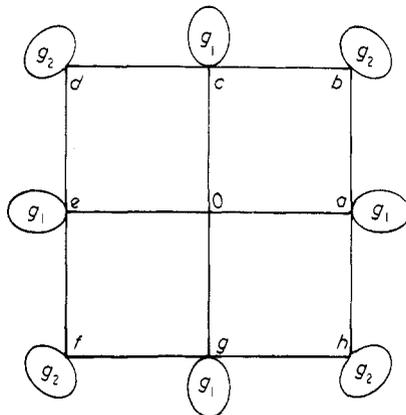


Figure 6. Diagram representing the effective hamiltonian in the cluster method.

shown in figure 6, where  $g_1$  and  $g_2$  represent the sum of all excursions into the surrounding medium only and returning to the same atom. We ignore the fact that one can get from one atom to another via the medium though this could be included in a further stage of elaboration. Let us define  $G_a$  as the sum of all chains from atom  $a$  and returning there without passing through atom zero;  $G_b$  as the sum from atom  $b$  not passing through atoms 0 and  $a$ ;  $G_c$  from atom  $c$  avoiding atoms 0,  $a$ ,  $b$ : etc. The following equations are then exact as regards all chains

$$\begin{aligned}
 G_{00}(E) &= \frac{1}{E - 4h^2G_a - 8h^4G_aG_bG_c - 8h^6G_aG_bG_cG_dG_e - 8h^8G_aG_bG_cG_dG_eG_fG_g} \\
 G_a &= \frac{1}{\frac{1}{g_1} - 2h^2G_b - 2h^8G_bG_cG_dG_eG_fG_gG_h} \\
 G_b &= \frac{1}{\frac{1}{g_2} - h^2G_c} & G_c &= \frac{1}{\frac{1}{g_1} - h^2G_d} \\
 G_d &= \frac{1}{\frac{1}{g_2} - h^2G_e} & G_e &= \frac{1}{\frac{1}{g_1} - h^2G_f} \\
 G_f &= \frac{1}{\frac{1}{g_2} - h^2G_g} & G_g &= \frac{1}{\frac{1}{g_1} - h^2G_h} \\
 G_h &= g_2.
 \end{aligned} \tag{2.16}$$

Now  $g_1$  and  $g_2$  have to be approximated to by some set of equations analogous to (2.12*b* and *c*). However if they are Herglotz, no matter what the approximation, they correspond to some real hamiltonian, that is to some real set of atoms which we can imagine hung on to each of the points in figure 6 instead of the real lattice. For example (2.8), (2.9) corresponds exactly to an ever branching snow crystal (see figure 4 of Weaire and Thorpe 1971). Thus the equations (2.16) are exact for some realizable system and  $G_{00}(E)$  should turn out Herglotz. It can be evaluated starting at the bottom and working upwards through the set of equations.

### 3. The recursion method

We proceed now to describe the best method of calculation we have arrived at, the 'recursion method'.

We define a mutually orthogonal set of states  $|n\rangle$  on the lattice, and assume for the present that we are dealing with an  $s$  band though the crystal structure can remain unspecified. As the first state  $|1\rangle$  we take the  $s$  state  $|0\rangle$  on the atom we are considering in (1.2*a*). The next state  $|2\rangle$  is defined by

$$|2\rangle = H|1\rangle - a_1|1\rangle \tag{3.1}$$

where the coefficient  $a_1$  is chosen to orthogonalize  $|2\rangle$  to  $|1\rangle$ . The higher  $|n\rangle$  are defined similarly by repeated operation with  $H$  and orthogonalizing to all previous  $|r\rangle$ ,  $r < n$ . We have

$$|n+1\rangle = H|n\rangle - a_n|n\rangle - b_{n-1}|n-1\rangle. \quad (3.2)$$

The interesting point about this formula is that  $H|n\rangle$  is automatically orthogonal to all the states  $|m\rangle$  with  $m < n-1$  so that these do not occur in (3.2). To prove this, consider  $\{m|H|n\rangle$ , the overlap of  $H|n\rangle$  with  $|m\rangle$ . Now the same matrix element can be regarded as the overlap of  $\{m|H$  with  $|n\rangle$ . Since  $\{m|H$  generates a linear combination of  $\{m+1|$  and other  $\{r|$  with  $r \leq m$ ,  $\{m|H|n\rangle$  is zero if  $m+1 < n$ . Note that the states  $|n\rangle$  defined by (3.2) are not normalized.

Some simple manipulation establishes the matrix elements  $H_{ij}$  of  $H$  in this basis, and the formulae for evaluating the  $a_n$  and  $b_n$ . Taking the product of (3.2) with  $\{n|$  and  $\{n-1|$  we have

$$H_{nn} = \frac{\{n|H|n\rangle}{\{n|n\rangle} = a_n \quad (3.3a)$$

$$H_{n-1,n} = \frac{\{n-1|H|n\rangle}{\{n-1|n-1\rangle^{1/2}\{n|n\rangle^{1/2}} = b_{n-1} \left( \frac{\{n-1|n-1\rangle}{\{n|n\rangle} \right)^{1/2}. \quad (3.4)$$

The latter matrix element can also be evaluated by operating  $\{n-1|H|n\rangle$  with  $H$  to the left,

$$H_{n-1,n} = \frac{\{n|n\rangle}{\{n-1|n-1\rangle^{1/2}\{n|n\rangle^{1/2}} = \left( \frac{\{n|n\rangle}{\{n-1|n-1\rangle} \right)^{1/2} \quad (3.5)$$

whence comparison with (3.4) gives

$$b_{n-1} = \frac{\{n|n\rangle}{\{n-1|n-1\rangle} \quad (3.3b)$$

$$H_{n-1,n} = H_{n,n-1} = [b_{n-1}]^{1/2}. \quad (3.3c)$$

The basis functions  $|n\rangle$  can be expressed in terms of the atomic orbitals  $|r\rangle$ ,

$$|n\rangle = \sum_r A_{nr} |r\rangle \quad (3.6)$$

and stored as column vectors  $A_{nr}$ . Then  $|n+1\rangle$  is obtained from (3.2) where  $a_n$  and  $b_{n-1}$  are defined by (3.3a), (3.3b).

All other matrix elements  $H_{nm}$  are zero, as follows also from (3.2).

$$H_{nm} = 0 \quad \text{for} \quad |n-m| > 1. \quad (3.3d)$$

Thus the matrix  $H_{nm}$  defined by (3.3) has tridiagonal form, and it follows quite simply by various arguments that the corresponding  $G_{00}$  equals the continued fraction (2.6) (Akhiezer 1965). Perhaps the easiest way in terms of the concepts of §2 is to note that  $H_{nm}$  is the hamiltonian of a fictitious line of 'atoms' with local orbitals  $|n\rangle$ , diagonal energies  $a_n$  and overlap matrix elements  $[b_n]^{1/2}$  to 'atom'  $n+1$  (figure 7). The important property of this fictitious line of 'atoms' is that for any given length, the contribution of closed walks on the original lattice, and on the (weighted) linear chain is the same. Because at each stage of the definition of the states  $|n\rangle$  the hamiltonian operates on all its nearest neighbours, exact computation of the states up to  $|N\rangle$  is equivalent to knowing

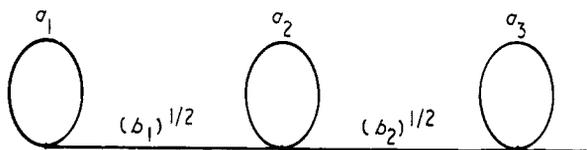


Figure 7. A line of fictitious 'atoms', equivalent to the hamiltonian in the representation (3.3)

the first  $2N$  moments. In the terms of §2, we have summed over all irreducible paths of length up to  $2N$  and all reducible paths that can be built up out of these. The argument of figure 3 and (2.8) then gives the following set of equations which are exact because the system is one dimensional:

$$\begin{aligned}
 G_{00} &= \frac{1}{E - a_1 - b_1 g_1(E)} \\
 g_1(E) &= \frac{1}{E - a_2 - b_2 g_2(E)} \\
 g_{n-1}(E) &= \frac{1}{E - a_n - b_n g_n(E)}.
 \end{aligned}
 \tag{3.7}$$

The substitution of these equations into one another immediately generates the continued fraction (2.6), which provides an exact solution to  $G_{00}(E)$  from which the density of states may be calculated using (1.2). As in the selfconsistent method, when the  $a_n, b_n$  have settled down to essentially constant values  $a, b$ , we can terminate the fraction with the function

$$g(E) = \frac{E - a}{2b} \left\{ 1 - \left( 1 - \frac{4b}{(E - a)^2} \right)^{1/2} \right\}
 \tag{3.8a}$$

analogous to (2.9), obtained by solving

$$g = \frac{1}{E - a - bg}.
 \tag{3.8b}$$

If we make this replacement at level  $n$ , the first  $2n$  moments of  $n(E)$  remain exact. Actually the limiting factor in the calculation is the number of atomic states that become involved as  $n$  increases, and we find much better than using (3.8) after  $n = 4$ , say, is to continue the process of (3.3) with a finite cluster of about 200 atoms to  $n$  of the order of 50. This catches long irreducible chains that wind around in the neighbourhood of the central atom, while ignoring a smaller number that would extend outside the cluster. For  $d$  bands in a FCC structure, we find agreement with the best conventional  $k$ -space calculations for the 10 main peaks in  $n(E)$ . The extension of the method to  $d$  bands will be published with results on surfaces (Haydock and Kelly 1972).

One minor mathematical point: in a system with symmetry, the functions  $|n\rangle$  do not form a complete basis set. By construction they all belong to the same irreducible representation of the symmetry group as  $|1\rangle = |0\rangle$  does, and they span the space of such functions on the lattice completely. Eigenfunctions of other symmetry have zero amplitude on atom zero and hence from (2.2) do not contribute to  $G_{00}$ . Our construction of  $G_{00}$  is therefore complete.

The representation of  $H$  in terms of the one dimensional array of figure 7 is not without physical significance. Since  $H|r\rangle$  generates the set of neighbouring orbitals to

$|r\rangle$ , the  $A_{nr}$  in (3.6) are zero beyond the planes of atoms  $n - 1$  steps from the origin. For the simple cubic lattice these define an octahedron. Thus  $|n\rangle$  represents the orbitals on this octahedral shell of atoms, its amplitude on the interior atoms being relatively small because of the orthogonalization. The representation (3.3) and figure 8 may be thought of as the one dimensional radial wave equation between shells.

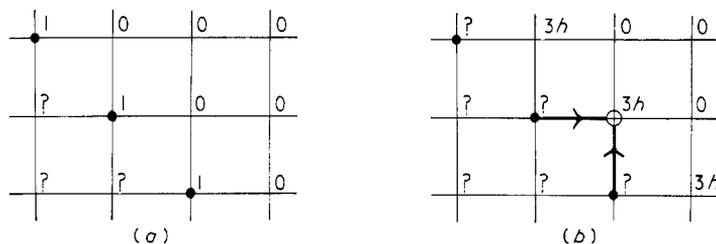


Figure 8. (a) Representation of the basic function  $|n\rangle$  in terms of the amplitudes  $A_{nr}$  on the atoms  $r$ . Those marked ? are irrelevant to the argument. (b) The same for  $|n - 1\rangle$ , the atoms denoted by heavy dots being the same as in (a).

One interesting small point remains to be tidied up. The simple cubic  $s$  band extends between the energies  $\pm 6h$  as already discussed in § 2. Thus  $a$  and  $b$  in (3.8) must be given by

$$a = 0 \quad b = 9h^2 \quad (3.9)$$

but it is not at first obvious how these limiting values arise from our recursion process (3.2, 3.3). The following didactic argument is not intended to be rigorous, merely to dispel any mystery. The result that all  $a_n$  are zero derives from the fact that only chains of even order exist on the simple cubic lattice. Thus all odd terms in (2.4) are zero and  $G_{00}(E)$  has to be an even function of  $E$ . The result for  $b$  is really  $(\frac{1}{2} \times 6h)^2$  where 6 is the number of nearest neighbours. Figure 8a shows the outer set of coefficients  $A_{nr}$ . Actually they are not exactly equal, but are proportional to the number of paths reaching a given atom from the origin and this is slowly varying at the centre of one of the faces of the octahedron. Also the outer  $A_{nr}$  do not have the value unity as shown, but some other constant: but since  $|n\rangle$  is an unnormalized function this does not matter: only the relation of  $|n + 1\rangle$  to  $|n\rangle$  matters in determining  $b_n$  from (3.3b). Figure 8b now shows the result of operating with  $H$  and this correctly represents the outer shell of  $|n + 1\rangle$  because the orthogonalizing terms in (3.2) do not affect the outermost shell. We see from figure 8b that  $|n + 1\rangle$  is a function of the same form as  $|n\rangle$  but with amplitude  $3h$ . The number 3 derives from the fact that a given outermost atom in  $|n + 1\rangle$  (large circle) can be reached from three outermost atoms of  $|n\rangle$ , two shown by arrows and the third from the third dimension. Then (3.3b) gives the value (3.9).

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