

THE ELECTRONIC STRUCTURE OF
TRANSITION METAL ALLOYS

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The calculation of the electronic structure of complex systems by traditional bandstructure methods is impractical and physically opaque. For such problems, the real space recursion method is a powerful computational tool. However, in the representation of the density of states, $n(E)$, as a continued fraction, an approximation must be made for the uncalculated tail of the fraction. A commonly used technique leads, for $n(E)$ and integrated quantities such as the total energy, to slow convergence with respect to the number of levels in the fraction, and does not preserve the moments of $n(E)$, which are implicitly calculated beforehand.

In this thesis, a new technique for terminating the fraction is presented. It is developed for bands with a single gap and with no gap, and surmounts most of the problems above. It is demonstrated on simple model bands and on the canonical d bands for the FCC, BCC and HCP structures, showing the superior convergence for $n(E)$ and the energy, and the preservation of the moments. For the canonical bands, the effects of cluster size are investigated and a general prescription for the length of the fraction to be used is developed. It is also found that the structural energy differences between the phases are driven by particular levels, indicating the relative importance of certain environments in the structural stability.

The new technique is then used in calculations of electronic structure in two areas of current interest.

Some insight into the behaviour of the complex alloy Y_4Co_3 - of interest for its magnetic and superconducting properties - may be gained by calculating the local electronic structure. On the basis of the local Stoner criterion, the method is unable to distinguish between two possible sites for the Co moment.

The crystal structures of the transition metal AB alloys can be analysed in two-dimensional structure maps, in which separation between structures can be achieved. The d band AB alloy structures calculated to be stable have been plotted in terms of N_A , N_B , the number of d electrons on each atomic species. A degree of separation is obtained which compares well with experimental data characterised by Pettifor's chemical scale.

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Chapter 1. Introduction

In this Chapter we present the reasons for using the real space recursion method in the calculation of the electronic structure of complex systems, and explain the basics of the theory underlying the method. A simple example of a two dimensional triangular lattice is used to illustrate the theory.

§1.1 Introduction

The theory of metals has traditionally been based on a reciprocal space representation of the electronic structure. The idealisation of perfect, infinite translational symmetry leads rigorously to Bloch's theorem and the concepts of wave vectors, energy bands and Brillouin zones. While yielding relatively clear, simple analytic descriptions of metallic behaviour, the reciprocal space formalism also provides sufficient calculational simplification to enable practical computation of realistic electronic structures. A great number of "bandstructure" methods have been developed; the increased availability of massive computer processing power encouraging the inclusion of greater complexity in the underlying physical models.

For each non-degenerate symmetry of electron orbital, the bandstructure methods produce a curve of $E(\underline{k})$ giving the energy, E , of an electron moving in the solid with wavevector $\underline{k}$. The collection of these dispersion relations for each of the non-degenerate symmetries - the bandstructure - provides a description of the electronic structure of the material. For many purposes, however, the more restricted information available from the density of states may be sufficient. To obtain the density of states the reciprocal space methods must calculate the full bandstructure, which they then sample to count levels in each energy interval. For the more complicated crystal structures such as Y_4Co_3 (see Chapter 5) these methods become increasingly impractical; in this particular magnetic compound there are 11 non-equivalent atomic positions each of which, in a tight

binding approximation, should have 10 exchange-split d orbitals associated with it. The bandstructure thus consists of 110 $E(\underline{k})$ curves.

A general feature of bandstructure methods, relevant to the work described in this thesis is that they do not necessarily give the correct moments, μ_n , of the density of states. Within the reciprocal space methods these moments are given in terms of sums over all wavevectors $\underline{k}$. In real computations, however, the sums can only be performed over some limited set of $\underline{k}$ points, and they do not then necessarily give the correct moments. By contrast, the real space methods described below should, by their very construction, necessarily give the correct moments.

Many situations in which there is little or no periodicity are of great current interest. Examples include the chemisorption of atoms onto surfaces, surface structure, liquids, amorphous materials and defects in bulk materials such as dislocations, impurities and vacancies. In all these areas there is a need for practical calculations of the electronic structure, but the lack of periodicity invalidates the basic premise of the bandstructure methods. The power of these methods is such, however, that it has been worth considerable effort to adapt them to be applicable to certain approximations to non-periodic cases. A consequence of the necessary complexity is often physical obscurity.

There is room here for relatively simple computational models which may allow qualitative or semi-quantitative exploration of these complex or non-periodic situations. In this thesis we examine one of these methods. Their essence lies in side-stepping reciprocal space

and working solely in real space. For this reason we will refer to them generally as "real space methods". Since they are not founded on Bloch's theorem, these methods are applicable to all periodic and non-periodic situations, although in the simpler periodic cases they are inevitably inferior to the bandstructure methods.

The particular method examined in this thesis is the "recursion method" developed in its present form by Haydock et al (1972, 1975 and see Solid State Physics 35 (1980)). Some details of its theoretical and computational basis are given in the following section.

In common with the "moments method" of Ducastelle and Cyrot-Lackmann (see section 1.2.4) the recursion method effectively attempts to calculate the electronic density of states by reconstruction from the moments

$$\mu_n = \int_{-\infty}^{\infty} E^n n(E) dE \quad (1.1.1)$$

If the moments can be calculated simply, this procedure avoids calculation of the full bandstructure and subsequent sampling. It is evident that, given a correct method of reconstruction from the input moments, this method does not suffer the failing of the bandstructure methods mentioned previously. Clearly, also, it may be possible for the moments to be calculated in a fashion independent from any reciprocal space formalism.

The power of the recursion method has been exploited for many calculations in the areas mentioned above where the bandstructure methods are infeasible due to low or absent periodicity (see, for example, Fujiwara 1979; Khanna et al 1979; Ballentine 1982; Sinai and Wu 1983). It has also been used to provide a simple calculational

scheme where the full power of the bandstructure methods might be inappropriate, for example the simple investigations of structural stability in Chapter 4.

In the remainder of this Chapter we present some of the theoretical and computational aspects of the recursion method, with the subsequent use of the method in mind. In Chapter 2 we begin by examining in some detail a common technique for the reconstruction of the density of states from the calculated recursion coefficients. The failings of this method provide the motivation for the development of the new technique described in the rest of Chapter 2 for connected bands and in Chapter 3 for bands with a single gap. These Chapters develop the theoretical basis of the new technique and use examples to demonstrate its efficacy. With the new technique we turn in Chapters 4 and 5 to applications. Structural stability of the pure transition metals and of the transition metal AB alloys is addressed in Chapter 4, while in Chapter 5 the magnetic structure of Y_4Co_3 , currently of great interest, is investigated.

§1.2 The Recursion Method.

The details of the recursion method are explained in this section. Haydock (1980) and companion authors in that volume have given a comprehensive review of the subject to which readers are referred for further detail than is provided here. Our coverage will be brief, but hopefully sufficient to introduce enough ideas to render the following Chapters comprehensible. We will, naturally, tend to focus attention on those aspects of the method that will prove to be important in later work.

Sections 1.2.1 and 1.2.3 are concerned with the details of the tridiagonalisation, the chain model and continued fractions and their representation of the density of states. In section 1.2.2 we use a simple example to illustrate the actual mechanics of the method. Finally, in section 1.2.4 we consider methods of calculating the coefficients using the moments of the density of states, principally as a means to obtain the continued fraction coefficients for model bands used in later Chapters. We discuss briefly the "moments method" used extensively by the French group of Cyrot-Lackmann, Ducastelle and co-workers (see 1.2.4). In that section we also present, for future reference, some details of the model and example bands that will be used throughout this thesis.

1.2.1 Tridiagonalisation and Chain Models

In a tight-binding representation the local density of states on an orbital $|\phi_0\rangle$ can be written

$$n(E) = - \frac{1}{\pi} \text{Im}(G_{00}(E)) \quad (1.2.1)$$

where the diagonal Greens function element is

$$G_{00}(E) = \langle \phi_0 | [E - H]^{-1} | \phi_0 \rangle \quad (1.2.2)$$

By E here is understood $E + i\varepsilon$ where the limit $\varepsilon \rightarrow 0^+$ is implied. The tight-binding Hamiltonian, H , is a sparse square matrix consisting of the elements $\langle \phi_\alpha | H | \phi_\alpha \rangle$ which are the energies E_α of the orbitals $|\phi_\alpha\rangle$ and the elements $\langle \phi_\alpha | H | \phi_\beta \rangle$ which are the hopping elements when $|\phi_\alpha\rangle$, $|\phi_\beta\rangle$ are close neighbours. We deal, for simplicity, throughout these sections with an orthonormal basis, $\langle \phi_\alpha | \phi_\beta \rangle = \delta_{\alpha\beta}$; the arguments can be generalised to non-orthogonal bases (Haydock 1980). From the whole of the Greens function, $G(E) = [E - H]^{-1}$, the local density of states requires only the diagonal element corresponding to the orbital of interest, called here $|\phi_0\rangle$. Direct inversion of the matrix $[E - H]$ is, of course, theoretically feasible, but this approach is practically impossible beyond small matrices and, moreover, yields vastly more information than we are interested in. It turns out that there is a simple and physically intuitive technique for evaluating only $G_{00}(E)$ (Haydock et al 1972, 1975; Haydock 1980).

We define a new basis set, $\{ |u_n\rangle \}$. These orbitals are linear combinations of the tight-binding basis orbitals,

$$|u_n\rangle = \sum_{m=0}^{\infty} c_{nm} |\phi_m\rangle \quad (1.2.3)$$

and are determined by the three term recurrence relation

$$b_{n+1}|u_{n+1}\rangle = (H - a_n)|u_n\rangle - b_n|u_{n-1}\rangle \quad (1.2.4)$$

where the a_n , b_n , b_{n+1} are constants. The recurrence is initialised with $|u_{-1}\rangle = 0$ and $|u_0\rangle = |\phi_0\rangle$ where particular choices of $|\phi_0\rangle$ are suitable for different calculations. For the local density of states on the orbital $|\phi_0\rangle$ we identify $|u_0\rangle = |\phi_0\rangle$ and the Greens function element (1.2.2) is then

$$G_{00}(E) = \langle u_0 | [E - H]^{-1} | u_0 \rangle \quad (1.2.5)$$

Consider, then, the first step in the recurrence (1.2.4) with $n = 0$. The tight-binding Hamiltonian connects the orbital $|u_0\rangle = |\phi_0\rangle$ with its neighbours, through the hopping elements $\langle \phi_\alpha | H | \phi_\beta \rangle$. Thus, with various constant factors, the new recursion orbital $|u_1\rangle$ will be composed of contributions, c_{nm} in (1.2.3), from the neighbours of $|\phi_0\rangle$. Similarly, $H|u_1\rangle$ will generate the orbital $|u_2\rangle$ spreading over more distant neighbours of $|\phi_0\rangle$. The Greens function element is thus decomposed into contributions coming from progressively more distant environments around the orbital, $|\phi_0\rangle$, of interest. On physical grounds, we would expect the contributions from the more distant environments to be correspondingly less important at $|\phi_0\rangle$.

The constant coefficients a_n , b_n , b_{n+1} in (1.2.4) are determined by orthogonalisation of $|u_{n+1}\rangle$ to $|u_n\rangle$ and $|u_{n-1}\rangle$ and normalisation of $|u_{n+1}\rangle$. Multiplying (1.2.4) from the left with $\langle u_n |$, $\langle u_{n-1} |$ and $\langle u_{n+1} |$ we obtain, if $\langle u_n | u_n \rangle = 1$,

$$\begin{aligned} \langle u_n | H | u_n \rangle &= a_n \\ \langle u_{n-1} | H | u_n \rangle &= b_{n-1} \end{aligned} \quad (1.2.6)$$

$$\langle u_n | H | u_{n+1} \rangle = b_{n+1}$$

and, since $|u_n\rangle$ is orthogonal to all $|u_m\rangle$ $m \neq n, n-1, n+1$ (Haydock 1980), all other elements of H in this basis are zero:

$$\langle u_m | H | u_n \rangle = 0 \quad m \neq n, n-1, n+1. \quad (1.2.7)$$

In the new basis, therefore, H is the tridiagonal matrix:

$$H = \begin{pmatrix} a_0 & b_1 & 0 & 0 & & \\ b_1 & a_1 & b_2 & 0 & & 0 \\ 0 & b_2 & a_2 & b_3 & & \\ 0 & 0 & b_3 & \ddots & \ddots & \\ & & & & \ddots & \\ & & & & & 0 \end{pmatrix} \quad (1.2.8)$$

We will discuss in 1.2.3 how the Greens function element may be simply calculated from this representation of the Hamiltonian.

This new basis gives us a simple picture of the solid. The Hamiltonian (1.2.8) is the Hamiltonian of a semi-infinite chain of "atoms", Figure 1.2.1, with which are associated the orbitals $|u_n\rangle$, representing different environments around $|u_0\rangle = |\phi_0\rangle$. The self energies are then a_n , and the hopping elements are b_n .

The operation of the recurrence (1.2.4) for a finite cluster must terminate when all of the information in the original tight-binding Hamiltonian is incorporated into the tridiagonal Hamiltonian. We would then find (to within the numerical accuracy) that some $b_n = 0$. This then would be an equally complete description of the cluster, whereas we are interested in an approximation to the bulk density of states.

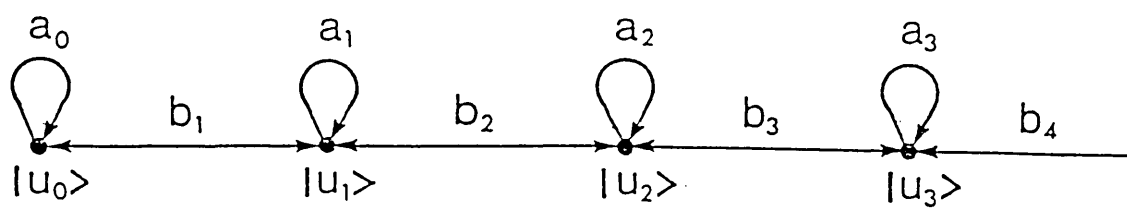


Figure 1.2.1 The Chain Model.

1.2.2 The Triangular Lattice.

To show explicitly the manner in which the recursion method works, we will manually perform here the first few steps of the tridiagonalisation for the triangular lattice with one tight-binding orbital per site. The resulting coefficients can be compared with those calculated numerically by Lambin and Gaspard (1982).

Part of the lattice is shown in Figure 1.2.2 with the chosen numbering for the orbitals. This system has been chosen because the sum of the magnitudes of the components of a vector gives the number of the "shell" in which that orbital lies. For example, $|\bar{1}20\rangle$ gives $1 + 2 = 3$ and this orbital is in the 3rd hexagonal "shell" around $|000\rangle$, requiring at least 3 nearest neighbour hops to be reached from the centre. The self energy of all sites is taken to be zero and the hopping element between nearest neighbours is h . We assume the tight-binding basis to be orthonormal.

The recursion procedure is initialised by setting $|0\rangle = |000\rangle$. This choice means that the chain model (equivalently the continued fraction (see 1.2.3)) generated by the recursion will be for the local density of states at orbital $|000\rangle$. We operate on $|0\rangle$ with H to obtain

$$H|0\rangle = h(|100\rangle + |010\rangle + |001\rangle + |\bar{1}00\rangle + |0\bar{1}0\rangle + |00\bar{1}\rangle) \quad (1.2.9)$$

The diagonal element, a_0 , is

$$a_0 = \langle 0|H|0\rangle = 0 \quad (1.2.10)$$

since $H|0\rangle$ does not have any weight on $|000\rangle$. The first of the recursion relations (1.2.4) gives

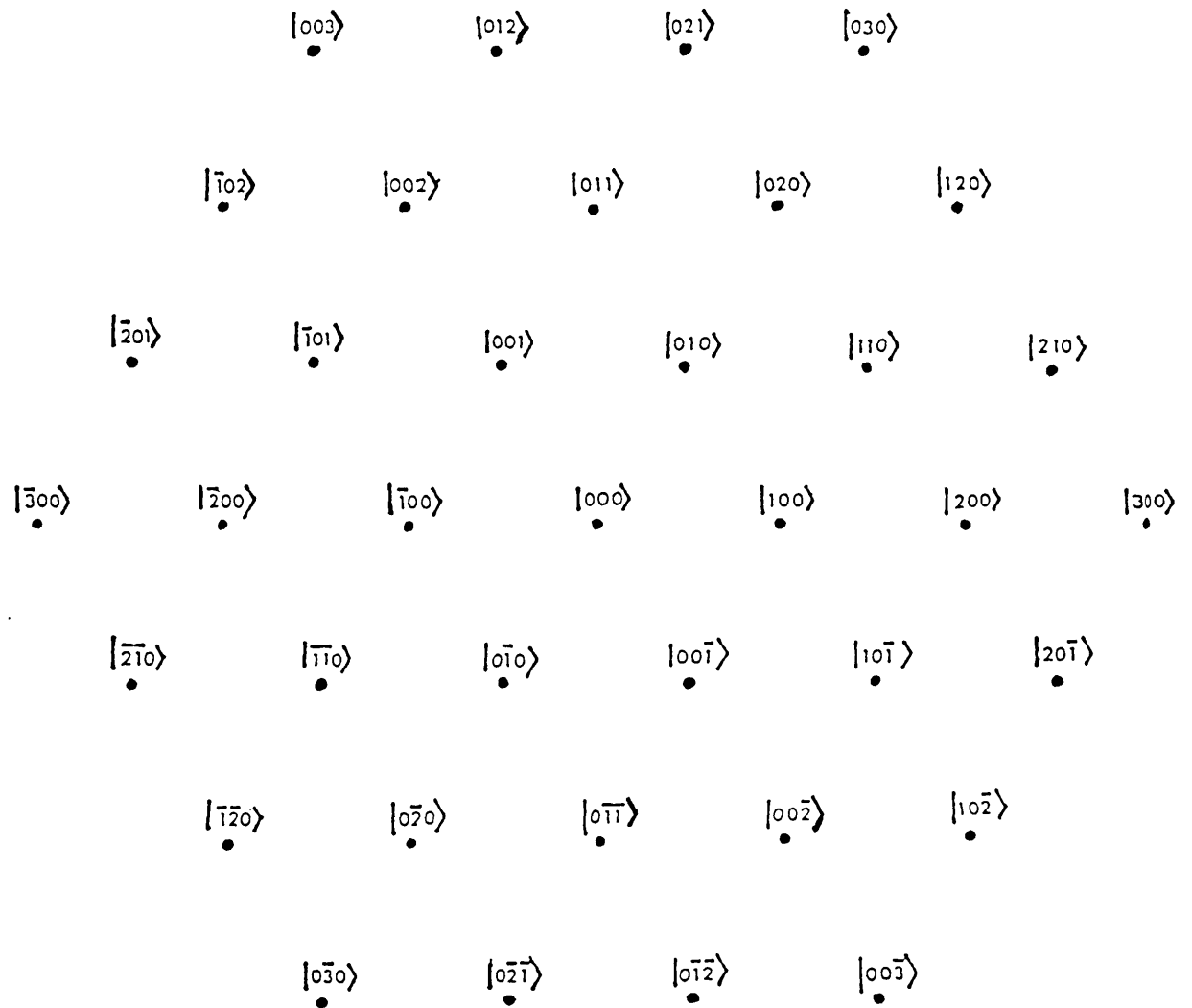


Figure 1.2.2 The Triangular Lattice.

$$b_1|1\rangle = H|0\rangle \quad (1.2.11)$$

so that b_1 is given by

$$b_1^2 = \{0|HH|0\rangle = 6h^2 \quad (1.2.12)$$

Before continuing with the next operation of H we introduce some notation that will simplify the expressions obtained. We denote by $|(lmn)\rangle$ the orbital $|lmn\rangle$ and the 5 other orbitals equivalent to it under the 6 fold rotational symmetry of the lattice. Thus (1.2.9) - (1.2.12) would be

$$\begin{aligned} H|0\rangle &= h|(100)\rangle \\ a_0 &= \{0|H|0\rangle = h\langle 000|(100)\rangle = 0 \\ b_1^2 &= \{0|HH|0\rangle = h^2\langle (100)|(100)\rangle = 6h^2 \end{aligned} \quad (1.2.13)$$

From (1.2.11) the orbital $|1\rangle$ is given by

$$|1\rangle = \frac{1}{\sqrt{6}} |(100)\rangle \quad (1.2.14)$$

Operation with the Hamiltonian on $|1\rangle$ then gives

$$H|1\rangle = \frac{h}{\sqrt{6}} (|(200)\rangle + 2|(100)\rangle + 6|000\rangle + 2|(110)\rangle) \quad (1.2.15)$$

whence

$$a_1 = \{1|H|1\rangle = \frac{h}{6} 2\langle (100)|(100)\rangle = 2h \quad (1.2.16)$$

The second of the recursion relations (1.2.4) is

$$b_2|2\rangle = (H - a_1)|1\rangle - b_1|0\rangle \quad (1.2.17)$$

We have the necessary terms on the right hand side and find, therefore,

$$\begin{aligned}
b_2|2\rangle &= \frac{h}{\sqrt{6}} (|(200)\rangle + 2|(100)\rangle + 6|000\rangle + 2|(110)\rangle) \\
&\quad - \frac{2h}{\sqrt{6}} |(100)\rangle - \sqrt{6}h|000\rangle \\
&= \frac{h}{\sqrt{6}} (|(200)\rangle + 2|(110)\rangle)
\end{aligned} \tag{1.2.18}$$

Normalising, we obtain

$$b_2^2 = \frac{h^2}{6} (\langle(200)|(200)\rangle + 4\langle(110)|(110)\rangle) = 5h^2 \tag{1.2.19}$$

$$|2\rangle = \frac{1}{\sqrt{30}} (|(200)\rangle + 2|(110)\rangle)$$

Notice here that $|2\rangle$ consists only of orbitals in the 2nd "shell" of nearest neighbours. We perform one more step in the tridiagonalisation: operation with H gives

$$\begin{aligned}
H|2\rangle &= \frac{h}{\sqrt{30}} (|(300)\rangle + 2|(110)\rangle + 3|(120)\rangle + 3|(210)\rangle \\
&\quad + 4|(200)\rangle + 5|(100)\rangle)
\end{aligned} \tag{1.2.20}$$

Then

$$\begin{aligned}
a_2 &= \{2|H|2\rangle = \frac{h}{30} (4\langle(200)|(200)\rangle + 4\langle(110)|(110)\rangle) \\
&= \frac{8}{5} h
\end{aligned} \tag{1.2.21}$$

From the third recursion relation

$$b_3|3\rangle = (H - a_2)|2\rangle - b_2|1\rangle \tag{1.2.22}$$

we find

$$\begin{aligned}
b_3|3\rangle &= \frac{h}{\sqrt{30}} (|(300)\rangle + 3|(120)\rangle + 3|(210)\rangle) \\
&\quad + \frac{6h}{5\sqrt{30}} (2|(200)\rangle - |(110)\rangle) \\
b_3^2 &= \frac{393}{75} h^2
\end{aligned} \tag{1.2.23}$$

We note that this orbital $|3\rangle$ is not confined only to the 3rd neighbour "shell", but also has non-zero weight on the 2nd. The orbitals $|n\rangle$ for $n > 5$ will have weight on all shells. The coefficients calculated here are listed in Table 1.2.1 and can be compared with those in Table IV of Lambin and Gaspard (1982).

1.2.3 Coefficients and Continued Fractions.

We now show how the coefficients a_n , b_n appearing in the recurrence relation (1.2.4) and determined by the orthonormality requirement on the orbitals $|u_n\rangle$ and the consequent tridiagonal representation of the Hamiltonian (1.2.8) are related to the diagonal element of the Greens function, and thence to the density of states. The leading diagonal element of $[E - H]^{-1}$, required by (1.2.2), is given by standard matrix algebra by the cofactor, D_1 , divided by the determinant, D_0 . We use here the notation that D_i is the determinant of $E - H$, where H is given by (1.2.8), with the first i rows and columns deleted. We can, however, expand the determinant D_n in the (remaining) first row or column to obtain

$$D_n = (E - a_n)D_{n+1} - b_{n+1}^2 D_{n+2} \tag{1.2.24}$$

i	a_i/h	b_i^2/h
0	0	6
1	2	5
2	$\frac{8}{5} = 1.6$	$\frac{393}{75} = 5.24$

Table 1.2.1 Coefficients for the
Triangular Lattice.

Thus, for example

$$\begin{aligned}
 \langle u_0 | [E - H]^{-1} | u_0 \rangle &= \frac{D_1}{D_0} \\
 &= \frac{D_1}{(E - a_0)D_1 - b_1^2 D_2} \\
 &= \frac{1}{E - a_0 - b_1^2 D_2 / D_1} \quad (1.2.25)
 \end{aligned}$$

Successive use of the determinant relation (1.2.24) leads to an expansion of the Greens function element as a continued fraction:

$$G_{00}(E) = \frac{b_0^2}{E - a_0 - \frac{b_1^2}{E - a_1 - \dots}} \quad (1.2.26)$$

b_0^2 is a normalisation factor for the density of states. We see, therefore, that the only information from the tridiagonalisation described in 1.2.1 required for the evaluation of the Greens function element is the set of coefficients a_i , b_i^2 . The higher coefficients determined by the more distant environments around $|u_0\rangle$ contribute to $G_{00}(E)$ in the "deeper" levels of the fraction. Their effect is correspondingly less (Wall 1948). We can thus appeal to the physical argument that the major dominant contributions will already have been included if we cease operating with the recurrence (1.2.4) at some finite and relatively small number of levels. In fact, it is vital that we truncate the fraction (1.2.26) (i.e. cease operating with (1.2.4)) at some level before the natural termination of $b_n = 0$ discussed in 1.2.1. One of the major features of the recursion method

is that until the orbitals $|u_n\rangle$ first include surface atoms at (say) the N th level, they are entirely unaffected by the surface of the cluster. Thus the first $N + 1$ pairs of coefficients a_i , b_i will have identical values to those calculated in an infinite cluster. We will often call these coefficients and orbitals "exact" since they have the bulk values. Now, with our cluster calculation we are attempting to find some approximation to the bulk density of states; if we continued including the coefficients beyond level N to the point where $b_n = 0$, then our fraction will be an exact representation of the cluster density of states, including all the surface and size effects. It has been argued (Haydock 1980; Haydock et al. 1975) that surface effects do not become important until a number of levels $\frac{3}{2}N < n < 5N$. Our results disagree with this conclusion and will be discussed in section 2.3.

If the fraction (1.2.26) is calculated to only a relatively small number of levels, r ,

$$G_{00}(E) = \frac{b_0^2}{E - a_0 - \frac{b_1^2}{E - a_1 - \dots \frac{b_r^2}{E - a_r}}} \quad (1.2.27)$$

then this approximation to the bulk density of states may be resolved into partial fractions:

$$G_{00}(E) = \sum_{i=0}^r \frac{w_i}{E - \epsilon_i} \quad (1.2.28)$$

If an imaginary part is included in E and then allowed to go to zero,

we obtain a spectrum of delta functions as the approximation to the density of states:

$$n(E) = \sum_{i=0}^r w_i \delta(E - \epsilon_i) \quad (1.2.29)$$

We know, however, that the bulk density of states will be composed of one or more continuous bands, and some form of continuous approximation to the bulk would be preferred to the delta function spectrum (1.2.29). Two methods of "smoothing" the spectrum (1.2.29) are discussed in detail in this thesis, both based on approximations of the effects that further (uncalculated) coefficients could have on $G_{00}(E)$. Note that the approximation here is not of further coefficients in the cluster, but of further coefficients in the bulk.

1.2.4 Other Methods for the Calculation of the Coefficients and the Example Bands.

The coefficients a_i , b_i in the continued fraction are related to the moments of the density of states,

$$\mu_n = \int_{-\infty}^{\infty} E^n n(E) dE \quad (1.2.30)$$

through (Turchi et al. 1982; Shohat and Tamarkin 1963):

$$a_n = \frac{1}{\Delta'_{n-1}} \left\{ \frac{\Delta_{n-1} \Delta'_n}{\Delta_n} + \frac{\Delta_n \Delta'_{n-2}}{\Delta_{n-1}} \right\} \quad (1.2.31)$$

$$b_n^2 = \frac{\Delta_n \Delta_{n-2}}{\Delta_{n-1}^2}$$

with $\Delta'_{-2} = 0$, $\Delta'_{-1} = \Delta_{-1} = 1$ and

$$\Delta_n = \begin{vmatrix} \mu_0 & \mu_1 & \dots & \mu_n \\ \mu_1 & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \mu_n & \mu_{n+1} & \dots & \mu_{2n} \end{vmatrix} \quad (1.2.32)$$

Δ'_n is of identical form to Δ_n but with μ_i replaced by μ_{i+1} . Thus a_0 is given by μ_1/μ_0 . Notice that the n th pair of coefficients, a_{n-1} , b_{n-1} , are functions only of the first $2n$ moments, $\mu_0, \dots, \mu_{2n-1}$. This means that if, out of a set of moments, the first $2n$ are exact then the first n levels of the corresponding coefficients will be exact, and vice versa.

The inverse relationship of the moments as functions of the coefficients can be expressed more simply. To the continued fraction

$$\frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \dots}} \quad (1.2.33)$$

corresponds (Wall 1948) a power series in descending powers of E ,

$$P(1/E) = \sum_{n=0}^{\infty} \frac{\mu_n}{E^{n+1}} \quad (1.2.34)$$

Expanding the fraction (1.2.33) into a power series (see Wall 1948 p203) gives

$$\begin{aligned}
& \frac{1}{E} + \frac{a_0}{E^2} + \frac{a_0^2 + b_1^2}{E^3} + \frac{a_0^3 + 2a_0b_1^2 + a_1b_1^2}{E^4} \\
& + \frac{a_0^4 + b_1^4 + b_1^2(a_1^2 + 2a_0a_1 + 3a_0^2) + b_1^2b_2^2}{E^5} + \dots \quad (1.2.35)
\end{aligned}$$

from which comparison with (1.2.34) gives the first few moments.

This relationship between the coefficients and the moments means that for simple model bands the coefficients in a continued fraction representation of the density of states can be determined from moments which are calculated exactly from simple analytic expressions. In Chapter 2, as examples of the application of our termination technique, we will use the continued fraction coefficients derived from the moments for the rectangular and skew rectangular bands shown in Figures 1.2.3 and 1.2.4. For reasons that will become apparent later, the parameters shown for the rectangular and skew rectangular bands have been chosen to fit the bands to, respectively, the first three and the first four canonical FCC moments (see below).

The computational algorithm used for the transformation to the coefficients is not a direct implementation of the relationship (1.2.31) and (1.2.32). We use instead a recursive algorithm (Wall 1948 p198) which avoids the difficulties due to the rapid increase with n of the magnitude of Δ_n . There are problems of numerical stability with both methods, which restrict us to calculating only about 20-25 pairs of coefficients.

For a tight-binding lattice, the moment μ_n can be written (Cyrot-Lackmann 1967) in terms of closed hopping paths of length n hops. The moments are thus relatively simply calculated for any tight-binding

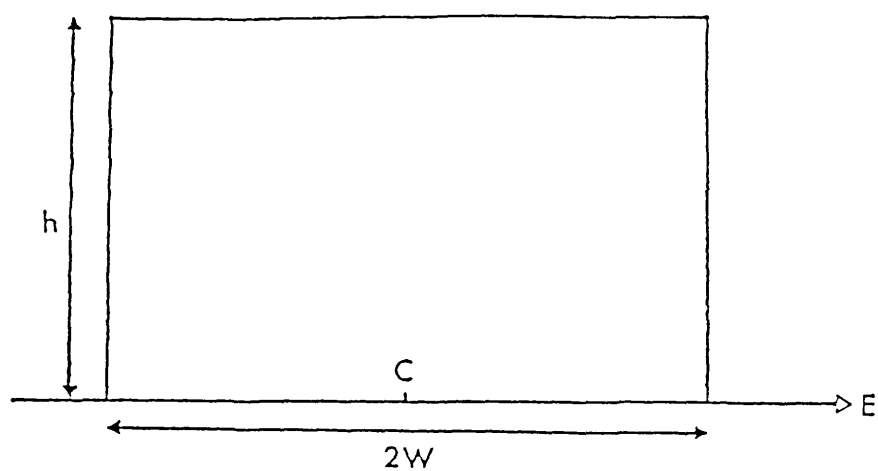


Figure 1.2.3 The rectangular density of states.
 Fitted to the first three FCC canonical moments
 the parameters are: $C = 0$, $W = 11.5756$,
 $h = 0.2160$.

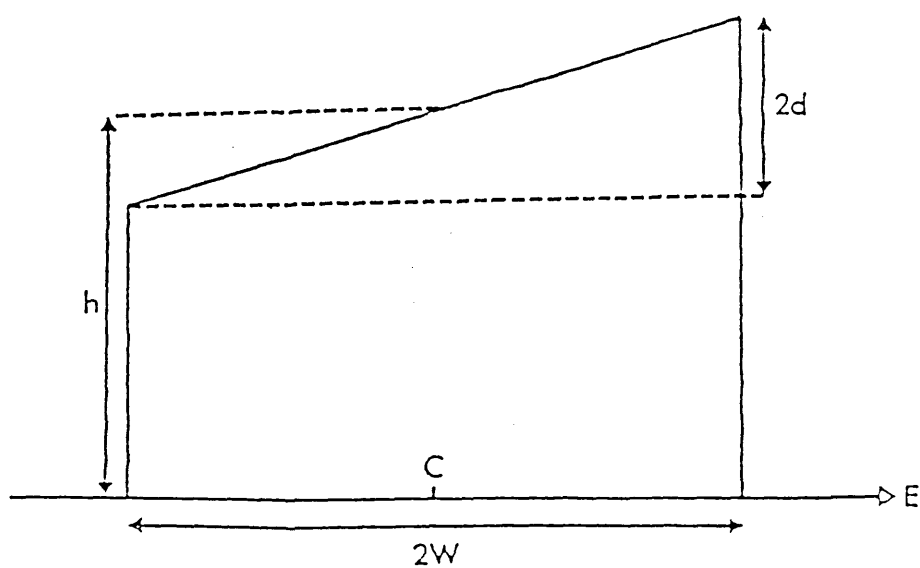


Figure 1.2.4 The skew rectangular density of states.
 Fitted to the first four FCC canonical moments
 the parameters are: $C = -1.3745$, $W = 11.8179$,
 $h = 0.2115$, $d = 0.0738$.

cluster. A model function can be fitted to the first few moments or the Gaussian quadrature for the integrated density of states can be constructed (Gaspard and Cyrot-Lackmann 1973; Gordon 1968,1969). The former method is no longer used, but allowed qualitative discussion of trends in transition metal properties (Cyrot-Lackmann 1968; Ducastelle and Cyrot-Lackmann 1970,1971; Cyrot-Lackmann and Ducastelle 1971). The latter method is closely related to the Cambridge method (Nex 1978) which will be discussed in detail in §2.1. In more recent work with the moment method (Desjonquieres and Cyrot-Lackmann 1974,1975,1976,1977) the moments are used to calculate the continued fraction coefficients and the density of states is calculated from these. This method has an advantage over the recursion method in that, since the moments are linearly related to the density of states (1.2.30), they may be configurationally averaged. The continued fraction coefficients derived from these moments will then describe a configurationally averaged density of states. The coefficients themselves are dependent on the density of states in a highly non-linear fashion and cannot, therefore, be averaged (Lambin and Gaspard 1982). The applications to liquids and disordered materials are immediate (Fujiwara 1979; Khanna et al. 1979; Ballentine 1982; Sinai et al. 1982; Sinai and Wu 1983). This advantage of the moments method is, of course, balanced by the numerical problems involved in the transformation to the continued fraction coefficients.

For the calculation of the coefficients direct from a cluster using the recursion method, we must specify, among other things, the interaction between neighbouring sites. This is done in terms of the Slater-Koster (1954) hopping parameters $dd\sigma$, $dd\pi$ and $dd\delta$. In all the examples and applications in this thesis we have used the canonical

form for these parameters (Andersen 1975; Pettifor 1977):

$$dd \begin{Bmatrix} \sigma \\ \pi \\ \delta \end{Bmatrix} = \begin{Bmatrix} -60 \\ 40 \\ -10 \end{Bmatrix} \frac{W_d}{25} (S/R)^5 \quad (1.2.36)$$

This choice leads to bands that do not depend on either the lattice constant or the d level energy, but only on the crystal structure (see Figure 1 of Andersen 1975). For the pure transition metals in the BCC, FCC and HCP structures we use $W_d = 25$ and set the d level energy to zero. To scale these canonical bands to a band of width W we simply multiply the energy scale by $25/W$, the density of states scale by $W/25$ and, if necessary, shift the band bodily by ϵ_d , the d level energy. As presented here, the energy E is equivalent to the dimensionless diagonalised canonical structure constant A , but, as indicated, the bands are simply scaled to suit individual cases.

For the transition metal compound Y_4Co_3 , studied in Chapter 5, we have taken the bandwidths W_d from the calculated bands of Moruzzi et al. (1978) for the pure constituents and the d level energies ϵ_d from Herman and Skillman (1963) for the atoms in the $d^{n+1}s^1$ configuration. The hopping parameters between Y and Co are taken to be the geometric mean of the Y-Y and Co-Co hopping (Shiba 1971). These choices for the parameters means that the values of the densities of states, Fermi energies etc. are directly applicable to a discussion of the properties of this material.

For the transition metal-transition metal AB alloys of Chapter 4, the value used for $W_d S^5/25$ in (1.2.36) is that for BCC niobium at its equilibrium atomic volume with a bandwidth of 10eV. This is a reasonably representative example for the transition metals.

The choices of parameters for the transition metal calculations will be discussed in detail in the sections dealing with the relevant calculations.

Chapter 2. The Connected Band

This Chapter presents the new termination technique, illustrates its application on simple examples and discusses the results obtained and practical aspects of its use.

As motivation for some of the following work we first describe in §2.1 the now commonly used Cambridge method and show results obtained with it for the example bands. In §2.2 the termination technique is then developed. We discuss the square root terminator appropriate to connected bands and detail the new technique for determining optimal parameters to be used in the terminator. The model bands are used to illustrate the general discussion. Comparisons are made at appropriate points between the results obtained with this new technique and those obtained with the Cambridge method: the considerably faster convergence of the structural energies and the preservation of the moments obtained with the new technique are particularly emphasised. Section 2.3 deals with the question of cluster size and the length of the continued fraction used, and develops a "rule of thumb" for guidance in practical situations. Finally, in §2.4, we draw together our conclusions about the use of the new technique.

§2.1 The Cambridge Method and its Problems

The Cambridge method (Nex 1978) has become a standard method for the reconstruction of densities of states and related integrated quantities from a finite number of continued fraction coefficients. The computer routines implementing the method, as available from Cambridge[†], are designed to be used as "black box" routines by Users totally or partially ignorant of their construction. Because of their widespread use, we have used this method as a reference against which to compare our termination method. In this section, therefore, we briefly explain how the method works and then demonstrate its efficacy in various situations.

We first show how the method reconstructs a density of states, $n(E)$, or an integral over $n(E)$ from the coefficients and then demonstrate its use on three simple bands which will also be used in later sections (these bands were described in detail in 1.2.4). Extensive study in 2.1.2 of the convergence of the density of states and the structural energy for these bands leads to the discussion in section 2.1.3 of a fundamental flaw in the method.

2.1.1 The Calculation of $n(E)$ and Integrated Quantities

The simplest approximation to the density of states is obtained by truncating the continued fraction representation of $G_{00}(E)$ at (say) r levels. This leads to the delta function spectrum of equation

[†] Cambridge Recursion Library available from C.M.M. Nex, Cavendish Laboratory, Cambridge, England.

(1.2.29). An integral of a function $f(E)$ over this spectrum is simply evaluated

$$F_r(E_F) = \int_{-\infty}^{E_F} f(E) n_r(E) dE = \sum_{i: \epsilon_i \leq E_F} f(\epsilon_i) w_i \quad (2.1.1)$$

but is not extremely useful since $F_r(E)$ will consist of a number, r , of steps at ϵ_i with height $f(\epsilon_i) w_i$. This approximation $N_r(E)$ to the integrated density of states is illustrated in Figure 2.1.1. It can be shown (Wall 1948) that the exact $N(E)$ crosses all the steps in $N_r(E)$; i.e.

$$\sum_{j: w_j < \epsilon_i} w_j \leq N(\epsilon_i - 0) \leq N(\epsilon_i + 0) \leq \sum_{j: w_j \leq \epsilon_i} w_j \quad (2.1.2)$$

as also shown in Figure 2.1.1.

A technique developed by Nex (1978) approximates $n(E)$ by smoothing (in some fashion) the r th level approximation to $N(E)$. We append a $\lambda(E)$ to the fraction:

$$G_{00}(E) = \frac{b_0^2}{E - a_0 - \frac{b_1^2}{E - a_1 - \dots \frac{b_r^2}{E - a_r - \lambda(E)}}} \quad (2.1.3)$$

where $\lambda(E)$ is determined so as to guarantee that the partial fraction expansion (1.2.28) for this fraction has precisely one pole, ϵ_i , at E . We then sum the $f(\epsilon_i) w_i$ over those poles with $\epsilon_i < E$ and find upper and lower bounds on $F_r(E)$ according to whether or not we include

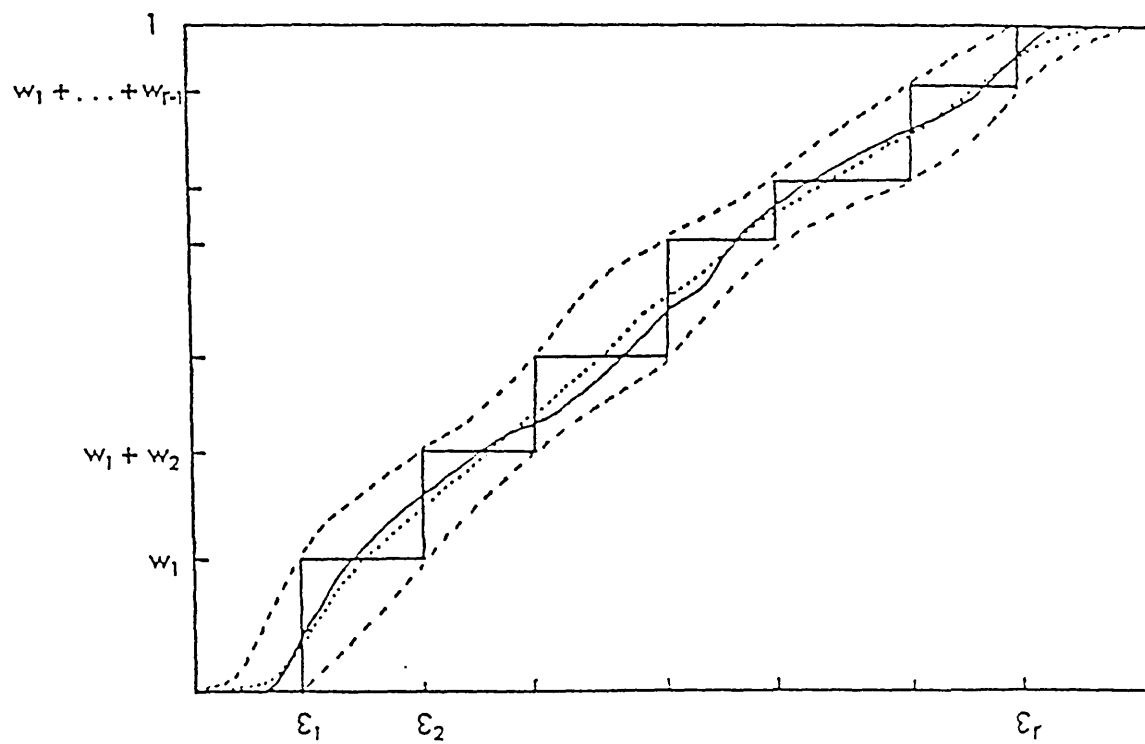


Figure 2.1.1 Step function approximation to $N(E)$.
(Cambridge Method).
 — exact $N(E)$
 - - - - - upper and lower bounds (2.1.7)
 average of bounds.

the contribution from the pole at E . These bounds rigorously include the exact $F(E)$ (Shohat and Tamarkin 1963, pp43,115) :

$$\sum_{i:\varepsilon_i < E} f(\varepsilon_i)w_i \leq F(E) \leq \sum_{i:\varepsilon_i \leq E} f(\varepsilon_i)w_i \quad (2.1.4)$$

Denoting the bounds by $F_{\pm}(E)$, we take as our approximation to the true $F(E)$ the mean of the bounds:

$$F(E) = \frac{1}{2} (F_+(E) + F_-(E)) \quad (2.1.5)$$

In other words, we include half the weight of the pole at E . The $\lambda(E)$ is an approximation for the effects of the uncalculated tail of the fraction, a_i, b_i , $i = r+1, \dots, \infty$, and the method used by Nex establishes rigorously the extremes of these effects. The density of states is then obtained by analytically or numerically differentiating the approximation to $N(E)$

$$n(E) = \frac{1}{2} \frac{d}{dE} (N_+(E) + N_-(E)) \quad (2.1.6)$$

These bounds and the average are also shown in Figure 2.1.1.

This method, implemented by Nex for the continued fraction coefficients, is closely related to methods deriving rigorous bounds directly from a knowledge of a finite number of the moments of a function (Gaspard and Cyrot-Lackmann 1973; Gordon 1968, 1969; Yndurain and Yndurain 1975). This is not totally unexpected in the light of the close relationship between the continued fraction coefficients and the moments.

2.1.2 Convergence Studies

The reliability of the density of states or related integral quantities obtained with the Cambridge method is studied here. By "reliability", we mean both the stability of the $n(E)$ (say) with changing numbers of levels in the fraction and the accuracy of the $n(E)$ when compared against the true, exact quantity. In practical situations, of course, we do not know the exact $n(E)$ and wish, therefore, to have confidence in an approximate calculation such as the Cambridge method provides. We would also desire the major features of the density of states to be reliably established with only a few levels and to remain as more levels are included in the calculation. This must be true if the method is truly to represent the effects of the local environment on properties such as the local density of states.

Use has been made of the Cambridge method in investigations of magnetic properties (Heine et al 1981; Samson 1982) in which a value for the density of states at the Fermi level, $n(E_F)$, plays a crucial role. Here, clearly, the accuracy of the method is vital. Other examples are provided by calculations of the energy differences between two structures or phases (see for example Burke 1976 and Chapter 4 of this thesis) or the "frozen phonon" calculations of Gale and Pettifor (1977) for the transition metal carbides.

As an investigation of the reliability of the Cambridge method, we present the density of states, $n(E)$, and the structural energy

$$U(E) = \int_{-\infty}^E E' n(E') dE' \quad (2.1.7)$$

as a function of band filling

$$N(E) = \int_{-\infty}^E n(E') dE' \quad (2.1.8)$$

obtained for the example bands of 1.2.4 for varying numbers of levels. In Figure 2.1.2 are shown the $n(E)$ for the rectangular band, and in Figure 2.1.3 the $n(E)$ for the skew rectangular band. In both cases, for few levels, the sharp band edges are not reproduced and there are considerable peaks throughout the band. A substantial number of levels would have to be used to achieve a good representation of the exact density of states.

In Figures 2.1.4 (a) - (d) are shown the $n(E)$ obtained using the FCC coefficients for varying numbers of levels. These curves are compared with the $n(E)$ obtained from a band structure calculation for first nearest neighbour canonical tight binding d bands (R. Muniz, private communication). For few levels (5-9), the Cambridge $n(E)$ have only the broadest of features in common with the "exact" $n(E)$, and between themselves there is considerable variation in the medium details such as the peak close to the upper band edge and the subsidiary peaks around $E \approx 6$. With further levels (11-15) the $n(E)$ seem to settle down to a stable form; there is little variation between them on energy scales of ≥ 2 . On comparison with the "exact" result, however, it is seen that this stable form is not a remarkably good representation of the bulk FCC $n(E)$; for example, the lower peaks at $E \approx -8$ and $E \approx -4$ are not resolved. With further levels the density of states seems to have reached a stable form, which is, however, still relatively structureless compared with the band structure result.

These results indicate that the $n(E)$ obtained with the Cambridge

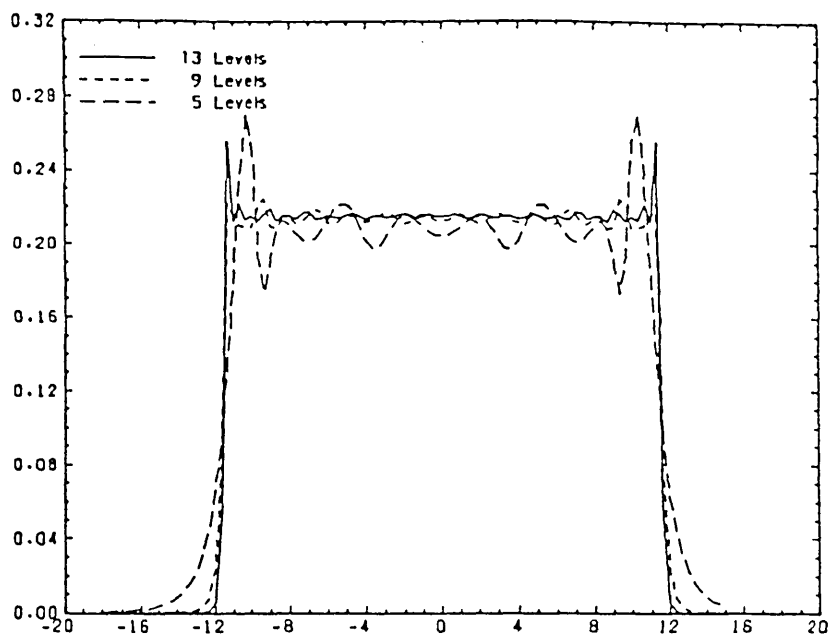


Figure 2.1.2 Convergence of the Cambridge approximation to the rectangular density of states.

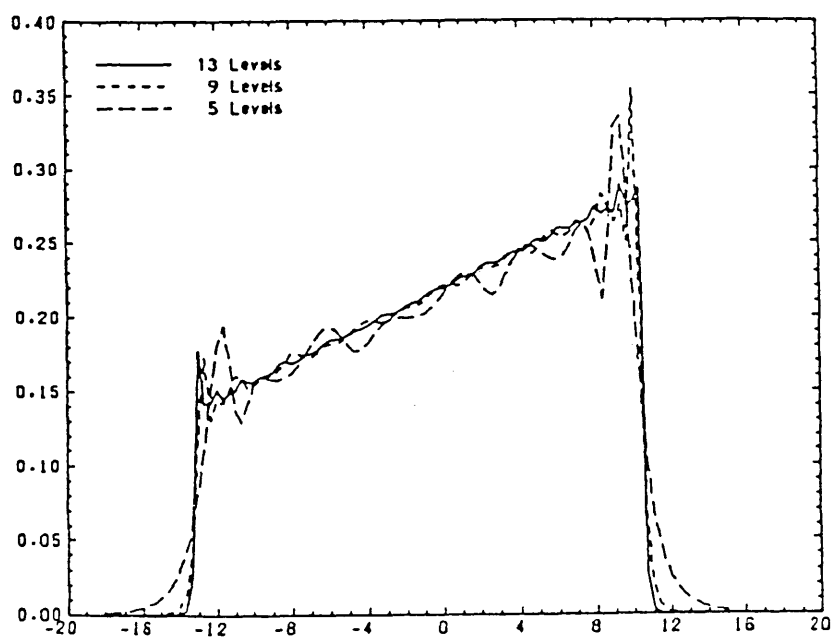


Figure 2.1.3 Convergence of the Cambridge approximation to the skew rectangular density of states.

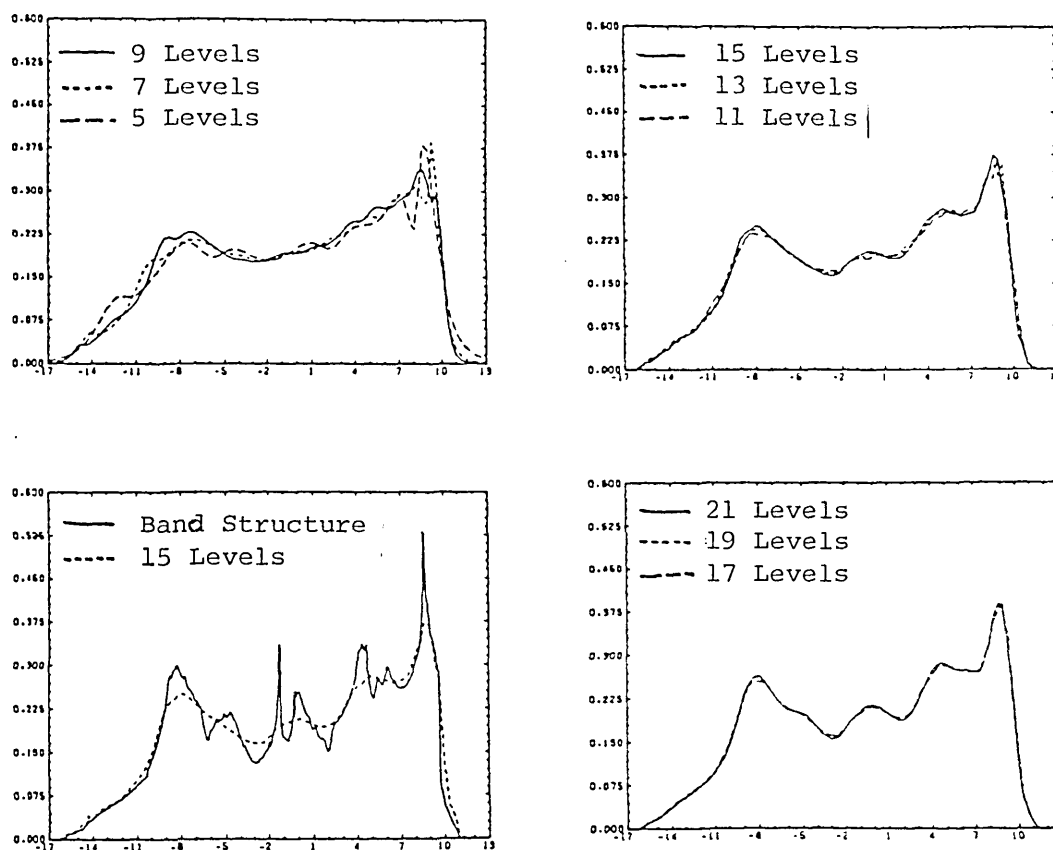


Figure 2.1.4

Convergence of the Cambridge approximation to the FCC density of states.

method are not reliable, since for few levels there is considerable variation in broad features between calculations with only slightly different numbers of levels, but, when with many levels the $n(E)$ are stable, they are not necessarily a good representation of the exact density of states.

Quantities which are integrals over the density of states are expected to be more quickly convergent than the density of states itself (Haydock 1980). We have therefore investigated the behaviour of the band structure energy, $U(N)$, given by (2.1.7) and (2.1.8). The energy for the rectangular band is shown in Figure 2.1.5 calculated with various numbers of levels. The calculated structural energies are approximately parabolic, but on this scale difficult to compare. In Figure 2.1.6 the calculated structural energy is shown relative to a reference $U_{\text{ref}}(N)$ which is the exact energy:

$$U(N) = -\frac{1}{2h} N(2hW - N) \quad (2.1.9)$$

This has the effect of removing the overall parabolic behaviour and emphasising the differences between the calculated $U(N)$ and the exact, and between calculations with different numbers of levels.

Although in Figure 2.1.6 we can see that there is some form of convergence towards the exact $U_{\text{ref}}(N)$ (i.e. $U(N) - U_{\text{ref}}(N) = 0$), we should also investigate the rigorous bounds on the structural energy difference. Since the true structural energy, $U_{\text{ref}}(N)$, crosses all the steps in the simple representation for $U(N)$, equation (2.1.4), we have

$$U_{-}(N) \leq U_{\text{ref}}(N) \leq U_{+}(N) \quad (2.1.10)$$

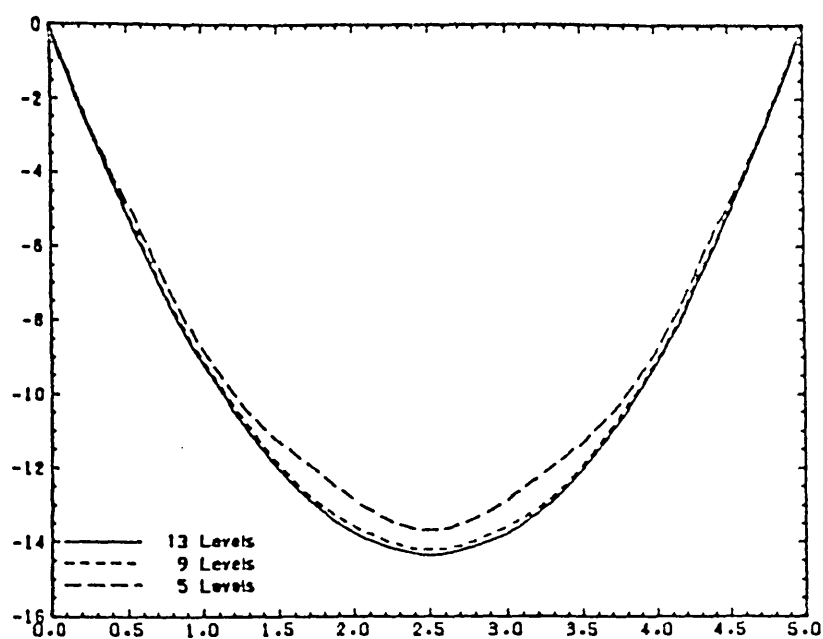


Figure 2.1.5 The structural energy of the rectangular band.
(Cambridge method).

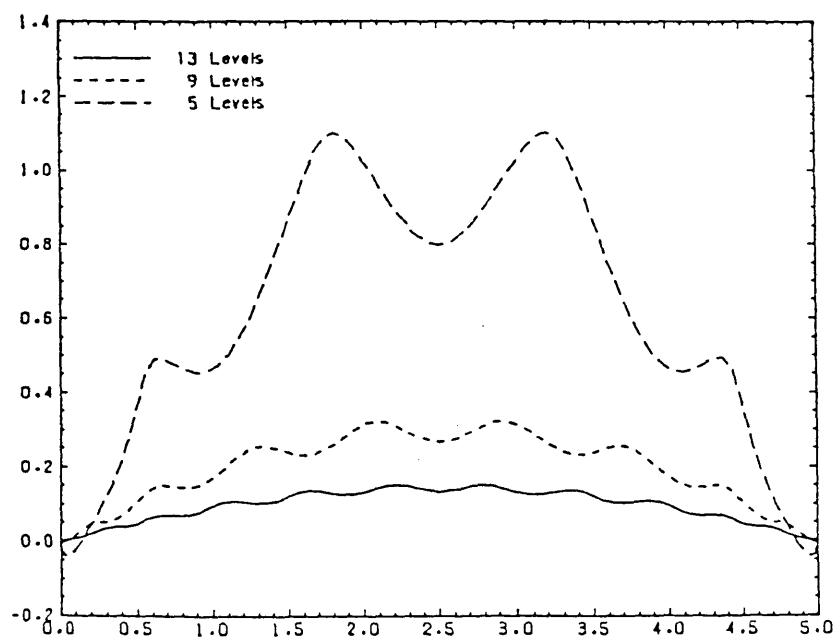


Figure 2.1.6 The structural energy of the rectangular band
relative to the exact energy. (Cambridge method).

Then, if $\Delta U_{\pm}(N)$ are the bounds on

$$\begin{aligned}\Delta U(N) &= U(N) - U_{\text{ref}}(N) \\ &= \frac{1}{2} (U_{+}(N) + U_{-}(N)) - U_{\text{ref}}(N)\end{aligned}\quad (2.1.11)$$

we find from (2.1.10) that

$$\begin{aligned}\Delta U_{+}(N) &> 0 \\ \Delta U_{-}(N) &< 0\end{aligned}\quad (2.1.12)$$

That is, no matter what the magnitude of $\Delta U(N)$, the maximum possible error always has a larger magnitude. With increasing numbers of levels these bounds converge slowly, as shown in Figure 2.1.7. The zero error at the centre of the band is due to the manner in which this method calculates the structural energy (Nex 1978).

The situation is very similar for the skew rectangular band. The $U(N)$ calculated are shown in Figure 2.1.8 relative to the exact structural energy given by the two equations:

$$U_{\text{ref}}(E) = \int_{C-W}^E E' \left(h + \frac{d}{W} (E' - C) \right) dE' \quad (2.1.13)$$

$$= -\frac{1}{2} \left(h - \frac{Cd}{W} \right) ((C - W)^2 - E^2) + \frac{d}{3W} (E^3 - (C - W)^3)$$

$$N(E) = \int_{C-W}^E \left(h + \frac{d}{W} (E' - C) \right) dE' \quad (2.1.14)$$

$$= -\left(h - \frac{Cd}{W} \right) ((C - W) - E) + \frac{d}{2W} (E^2 - (C - W)^2)$$

In Figure 2.1.9 the convergence of the bounds $\Delta U_{\pm}(N)$ with increasing numbers of levels are shown.

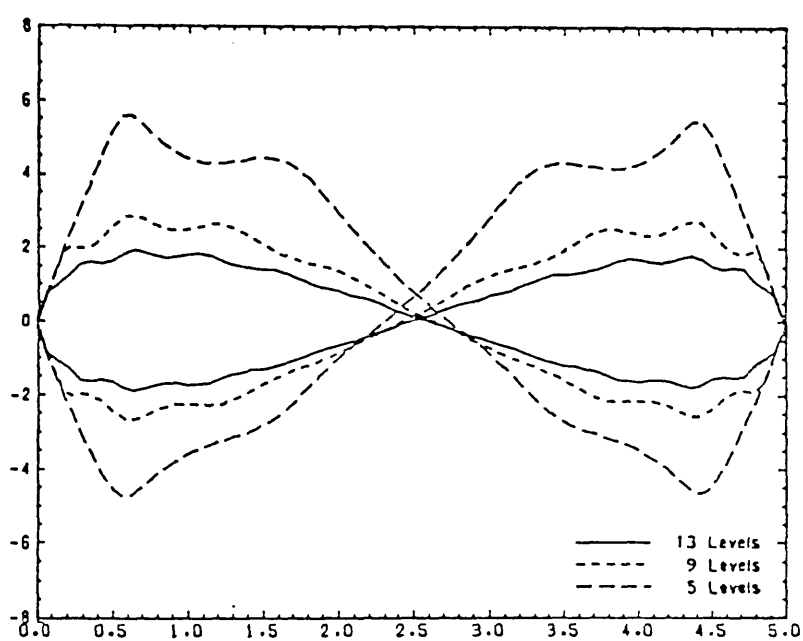


Figure 2.1.7 Convergence of the rigorous bounds $\Delta U_{\pm}(N)$ for the rectangular band. (Cambridge method).

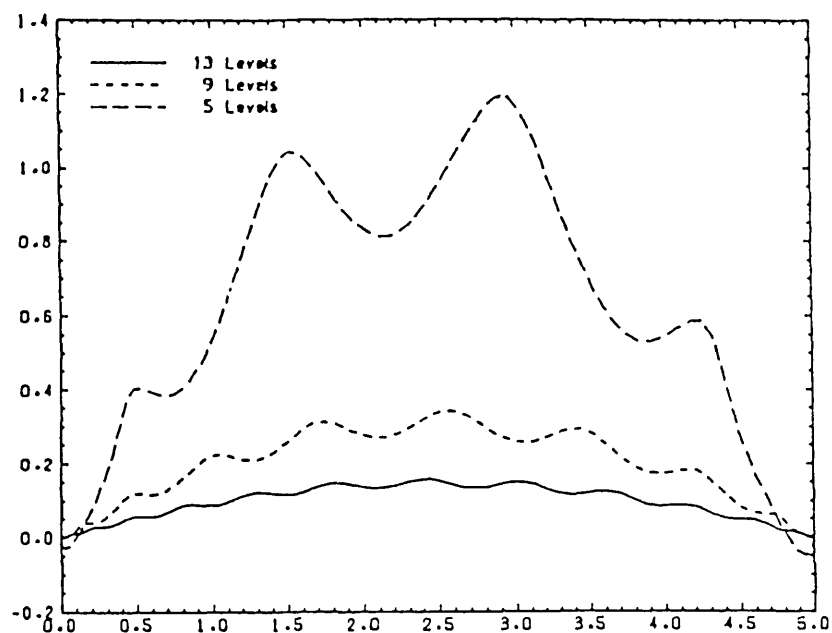


Figure 2.1.8 Structural energy of the skew rectangular band relative to the exact energy. (Cambridge method).

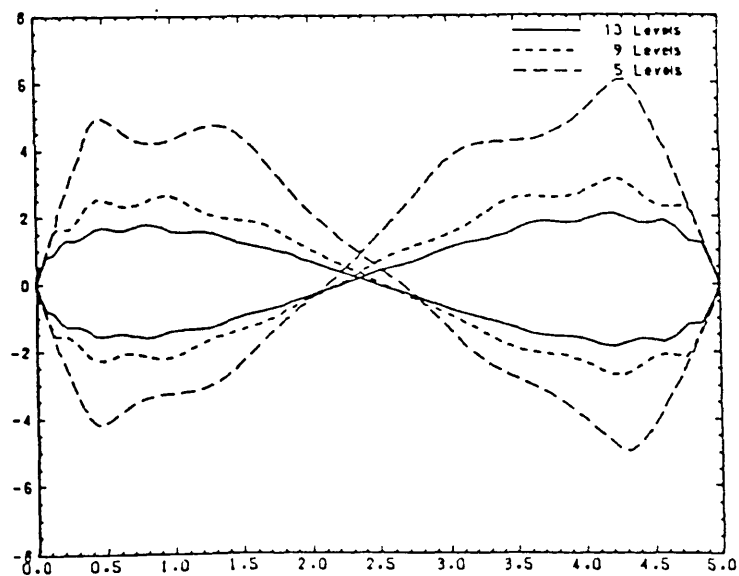


Figure 2.1.9 Convergence of the rigorous bounds $\Delta U_L(N)$ for the skew rectangular band. (Cambridge method).

For the FCC band (and also BCC and HCP) the structural energy is approximately parabolic. We remove this parabolic part and emphasise the structure dependent part of $U(N)$ by using the exact skew rectangular band $U(N)$ as a reference. This is the reason that the skew rectangular band was fitted to the first four FCC moments. The $\Delta U(N)$ calculated with the Cambridge method for various numbers of levels are shown in Figure 2.1.10. Once again, the convergence of these $\Delta U(N)$ towards a final form is slow. We note that the argument given above concerning the rigorous bounds on $\Delta U(N)$ is not applicable here since the reference $U(N)$ is derived from a totally different band.

2.1.3 The Moments of the Density of States

A simple theorem (Ducastelle and Cyrot-Lackmann 1971) enables us to establish a rigorous condition that the structural energy differences of Figures 2.1.6, 2.1.8 and 2.1.10 must obey.

If a function, $f_0(E)$, non-zero on $[E_b, E_t]$, with

$$f_0(E_b) = f_0(E_t) = 0 \quad (2.1.15)$$

has the first n of its moments

$$\mu_p = \int_{E_b}^{E_t} E^p f_0(E) dE \quad (2.1.16)$$

equal to zero (i.e. $\mu_p = 0$, $p \leq n-1$) then $f_0(E)$ must have at least n zeros in the region $[E_b, E_t]$ distinct from the end points. Moreover, if

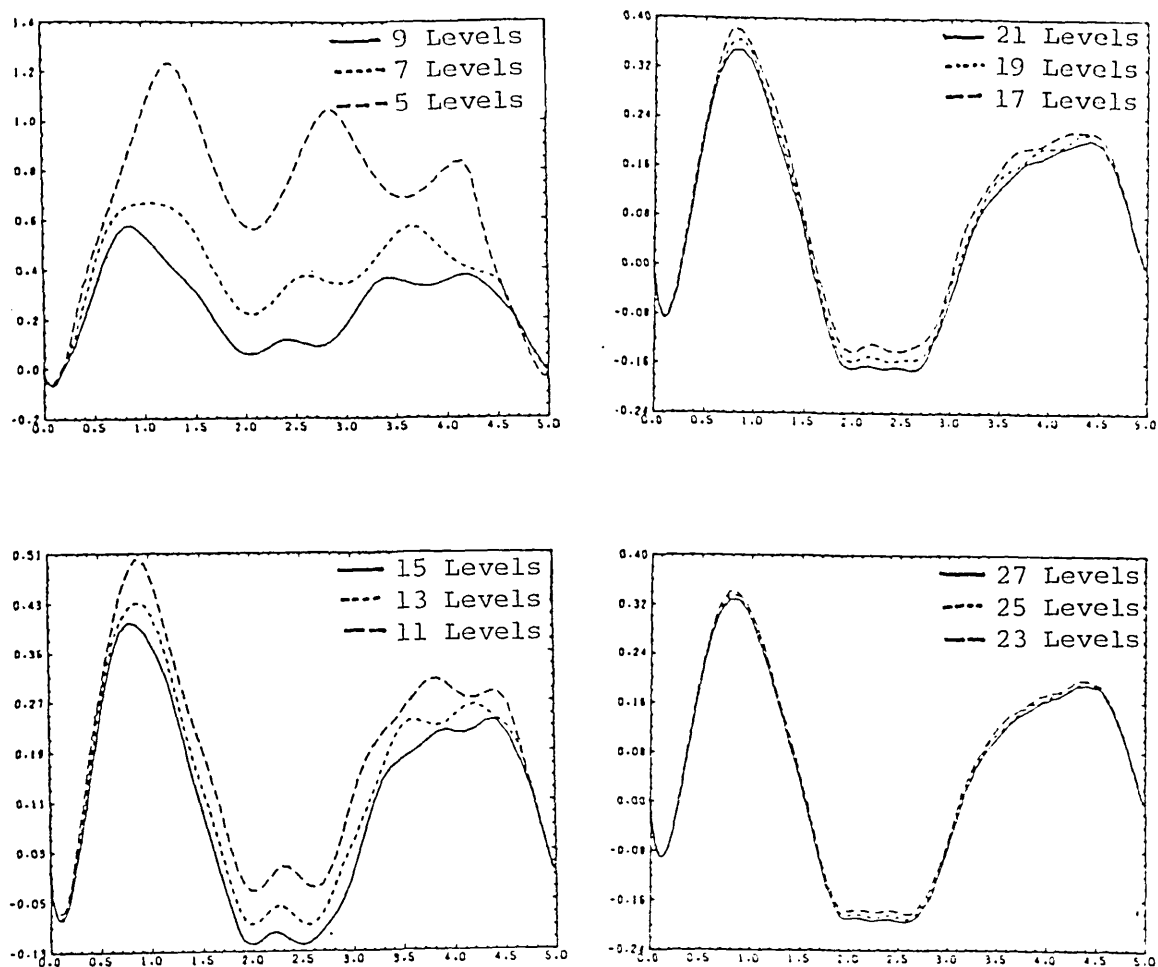


Figure 2.1.10 FCC structural energy relative to the exact skew rectangular energy. (Cambridge method).

$$f_q(E) = \int_{E_b}^E f_{q-1}(E') dE' \quad (2.1.17)$$

then $f_q(E)$ must have at least $n-q$ zeros distinct from E_b , E_t .

If, therefore, we form the difference of two functions which have their first n moments identical, this difference must have at least n zeros, or, equivalently, one function must oscillate about the other at least n times. This theorem allowed Ducastelle and Cyrot-Lackmann (1971) to discuss qualitatively the cohesive energy difference between the FCC and HCP structures across the transition metal series. Heine et al (1981) have used the theorem in their investigation of the phase diagram for disordered local magnetic moments. In the case of the FCC structural energy relative to the skew rectangular, the densities of states have their first four moments identical. Therefore, since

$$\int_{-\infty}^E (E' - E) n(E') dE' = \int_{-\infty}^E \int_{-\infty}^{E'} n(E'') dE'' dE' \quad (2.1.18)$$

the graphs in Figure 2.1.10 must have at least $4 - 2 = 2$ zeros distinct from the band edges. Similarly, in Figures 2.1.6 and 2.1.8, when we compare the $U(N)$ calculated with n levels, which has, therefore, the first $2n$ moments exact, with the exact $U(N)$, for which all moments are exact, then the resulting structural energy must have at least $2n-2$ zeros distinct from the band edges.

Inspection of these Figures reveals, however, that in some cases this rigorous requirement is not satisfied.

This result indicates the existence of a fundamental flaw in the Cambridge method. As mentioned in 1.2.4, the continued fraction coefficients are closely related to the moments: if n pairs of

coefficients are exact, then $2n$ moments are implicitly known exactly. For the rectangular and skew rectangular bands all the coefficients are exact, so, if we calculate with n levels, the resulting $n(E)$ should have its first $2n$ moments correct. For the FCC band, 20 pairs of the coefficients are exact. Thus in all three cases, the Cambridge method has begun with information about the density of states equivalent to the first $2n$ moments ($n \leq 20$), but it then fails to incorporate all of this into the $n(E)$ generated.

Consider the fraction (1.2.27) truncated at the n th level. The value of this fraction is given by the ratio of two polynomials, $P_n(E)/Q_n(E)$ in the notation of Haydock (1980), which individually satisfy three term recurrence relations (Haydock 1980). This ratio is called the n th approximant to the value of the infinite fraction (Wall 1948), and approximates the infinite fraction in the sense (Wall 1948 §42) that its expansion in descending powers of E ,

$$\frac{P_n(E)}{Q_n(E)} = \sum_{m=0}^{2n-1} \frac{c_m}{E^{m+1}} + \sum_{p=2n}^{\infty} \frac{c_p^{(2n)}}{E^{p+1}} \quad (2.1.19)$$

agrees term by term with the expansion in descending powers of E of the infinite fraction for the first $2n$ terms. But in the power series expansion of the infinite fraction (1.2.34),

$$P(1/E) = \sum_{m=0}^{\infty} \frac{\mu_m}{E^{m+1}} \quad (2.1.20)$$

the coefficients are the moments, μ_m , of the fraction. The n th approximant, therefore, gives correctly the first $2n$ moments. The

expansion (2.1.19) of the approximant requires that the polynomials $P_n(E)$ satisfy an orthogonality condition with respect to the density of states (Wall 1948; Haydock 1980) :

$$\int_{-\infty}^{\infty} P_i(E) P_j(E) n(E) dE = \delta_{ij} \quad (2.1.21)$$

Now consider the fraction (2.1.3) where, according to Nex (1978), we append a $\lambda(E)$ at the n th level. It is clearly required, if the correspondence between this fraction and the power series expansion (2.1.19) is still to hold, that $\lambda(E)$ must have the form of a continued fraction

$$\lambda(E) = \frac{\beta_{n+1}^2}{E - \alpha_{n+1} - \frac{\beta_{n+1}^2}{E - \alpha_{n+2} - \frac{\beta_{n+2}^2}{E - \alpha_{n+3} - \dots}}} \quad (2.1.22)$$

Then, for the p th approximant ($p > n$), the continued fraction coefficients α_{n+1} , β_{n+1} , α_{n+2} , ... contribute only to the terms in (2.1.19) of order E^{m+1} where $m > 2n$. For a simple two level fraction we can find an explicit form for $\lambda(E)$ and investigate whether it is a continued fraction of the form (2.1.22). Taking

$$G_{00}(E) = \frac{1}{E - a - \frac{b^2}{E - \lambda}} = \frac{E - \lambda}{(E - a)(E - \lambda) - b^2} \quad (2.1.23)$$

the requirement that $G_{00}(E)$ must have a pole at E gives

$$\lambda(E) = E - \frac{b^2}{E - a} \quad (2.1.24)$$

This cannot be put in the form (2.1.22) and thus by the argument above the correspondence between the power series expansion of the fraction (2.1.3) and the power series expansion of the true, infinite fraction, (2.1.20) does not hold. That is, the moments of (2.1.3) are not necessarily the moments of the true density of states included originally in the n th approximant (2.1.19). An alternative way of seeing this is by putting $\lambda(E)$ into continued fraction form but with energy-dependent coefficients:

$$\lambda(E) = \frac{\beta^2}{E - a}$$

$$\beta^2 = E(E - a) - b^2 \quad (2.1.25)$$

This energy-dependent coefficient in the recursion relation for the $P_n(E)$ means that the orthogonality requirement (2.1.21) will not be satisfied for all i, j and this in turn means that the correspondence between the continued fraction and the power series does not hold.

§2.2 The Square Root Termination Technique

We deal in this section with a method for the reconstruction of the density of states alternative to the Cambridge method described and demonstrated in §2.1. Our hope is that, properly applied, this technique - the square root termination technique - may be able to surmount some or all of the problems mentioned as affecting the Cambridge method.

We begin by describing what the square root terminator is and what assumptions about the behaviour of the coefficients are necessary

for its use. In 2.2.2 we start the development of the new technique for determination of the terminating parameters. The elements of the technique described in this section are demonstrated on the coefficients for the rectangular band of 1.2.4 which provides examples of the general development in the text. The technique is expounded in full detail in 2.2.3 with reference to the skew rectangular band. Finally, an example of a "real" application is given by demonstrating the use of the technique on the canonical FCC band of 1.2.4 .

The results obtained with this new technique are compared as appropriate with those obtained in §2.1 with the Cambridge method, with particular reference to any alleviation of the problems described for the latter method.

2.2.1 The Square Root Terminator

In the Cambridge method described in 2.1.1 the effects of the uncalculated coefficients in the tail of the fraction are ignored - the $\lambda(E)$ introduced in (2.1.3) does, however, allow rigorous limits to be established on these effects. We describe here an alternative technique for approximating the tail of the fraction. It is well known (Haydock et al 1975 ; Turchi et al 1982) that for a simply connected band (one without any band gaps) the exact continued fraction coefficients converge towards asymptotic limits a_∞ , b_∞ and that these are related to the bulk band edges by

$$E_t = a_\infty + 2b_\infty \quad , \quad E_b = a_\infty - 2b_\infty \quad (2.2.1)$$

The coefficients for the skew rectangular band, for example, plotted in Figure 2.2.1, converge rapidly towards the asymptotic values, while, in contrast, the coefficients for the FCC band (of which 20 pairs are exact) plotted in Figure 2.2.2, although generally convergent towards some asymptotic limit, still show considerable variation at the 20th level.

Because of this asymptotic behaviour of the coefficients, the approximation that is made for the tail of the fraction, a_i, b_i , $i = N+1, \dots$, is to replace all these coefficients by constant coefficients a, b , so that the fraction is then

$$G_{00}(E) = \frac{b_0^2}{E - a_0 - \frac{b_1^2}{E - a_1 - \dots \frac{b_N^2}{E - a_N - t(E)}}} \quad (2.2.2)$$

where

$$\begin{aligned} t(E) &= \frac{b^2}{E - a - \frac{b^2}{E - a - \dots}} \\ &= \frac{b^2}{E - a - t(E)} \end{aligned} \quad (2.2.3)$$

We can, therefore, find an analytic expression for the terminator $t(E)$:

$$t(E) = \frac{1}{2} \{E - a - \sqrt{(E - a)^2 - 4b^2}\} \quad (2.2.4)$$

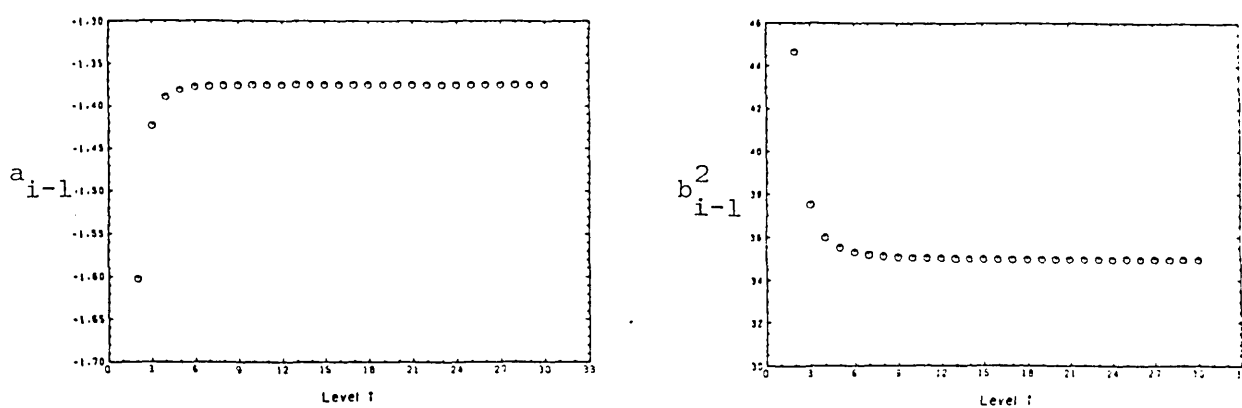


Figure 2.2.1 The skew rectangular band coefficients.

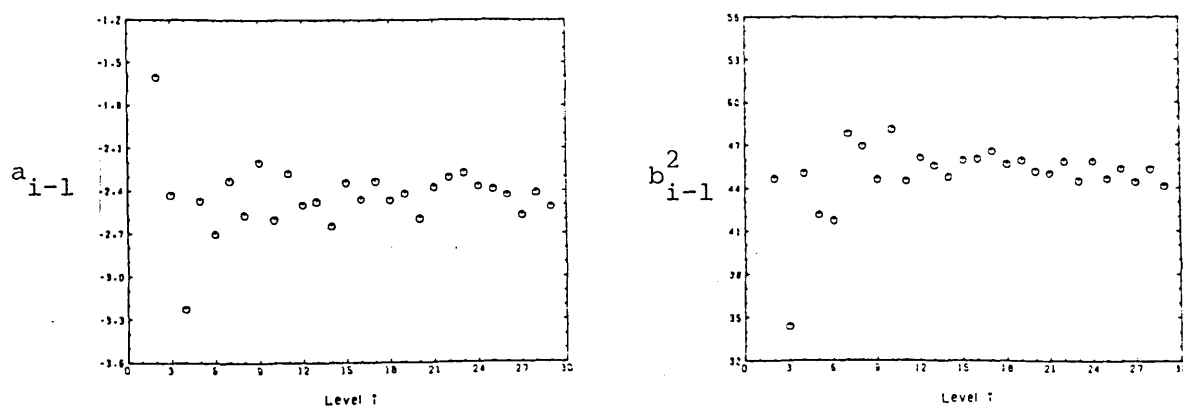


Figure 2.2.2 The FCC "average" coefficients.

This is the "square root terminator" (Haydock et al 1972,1975), which produces a cut on the real axis of the complex energy plane between $a - 2b$ and $a + 2b$. The second solution of the quadratic is rejected because $t(E)$ must vanish as $E \rightarrow \infty$ so that the fraction $G_{00}(E)$ preserves its analytic character of $1/E$ there. On this cut $t(E)$ is complex and thus gives rise to a connected spectrum for $n(E)$. Outside the limits $a \pm 2b$ the terminator is real and $n(E)$ is therefore zero, except for isolated delta functions where the real part of $G_{00}(E)$ changes sign (since the real and imaginary parts are connected by the Kramers-Kronig relations).

We are left, however, with two unknown parameters a , b which must be entered into the terminator. If we know the bulk band edges then we can enter the corresponding a_∞ , b_∞ , determined through (2.2.1). In some cases - the rectangular and skew rectangular bands for example - the coefficients are so quickly convergent that a good estimate of the asymptotic limits a_∞ , b_∞ may be made. More often, though, we do not know the bulk band edges and the coefficients are not quickly convergent enough to allow us to estimate a_∞ , b_∞ with much confidence. In this situation there is little to help our choice of the terminating parameters except some basic indication (Haydock et al 1975) of the consequences of choosing the bandwidth, $4b$, too large or too small.

Despite this difficulty, the square root terminator has been used in a number of applications. In their investigation of the structure of the transition metal Laves phases Haydock and Johannes (1975) entered a , b into the terminator as the average of the last two calculated coefficients. Cubiotti and Ginatempo (1980), studying H chemisorption on a Cu surface, estimated values for a_∞ , b_∞ from the

behaviour of 10 pairs of coefficients. Fujiwara (1979) also estimated a_{∞} , b_{∞} from 15 pairs of coefficients in his study of amorphous and liquid Fe, Co and Ni.

In this work, we view the terminating coefficients a , b as adjustable parameters, for which values will be uniquely determined according to a criterion developed in the next section.

2.2.2 The Bandwidth Criterion and the Finite Terminated Fraction

For this initial development of the termination technique we use the rectangular band (Figure 1.2.3) as an example. This band has been chosen because $a_i = 0$ for all i , due to the vanishing of the odd moments of the density of states. This implies that the terminating parameter a will also vanish. For the rest of this section we will assume that $a = 0$ and talk only in terms of the bandwidth and the parameter b . Haydock et al (1975) indicate briefly the effects of an incorrect choice of the bandwidth; we demonstrate here in detail the consequences of particular choices for b . We calculate the weight in the band,

$$\mu_0 = \int_{-\infty}^{\infty} n(E) dE \quad (2.2.5)$$

as a function of the terminating coefficient b . The density of states is calculated from the terminated fraction (2.2.2) and the integral performed numerically. The dependence on the parameter b of the weight in the rectangular band for 8 levels is shown in Figure 2.2.3. The consequence of choosing b too small is that the numerical integral

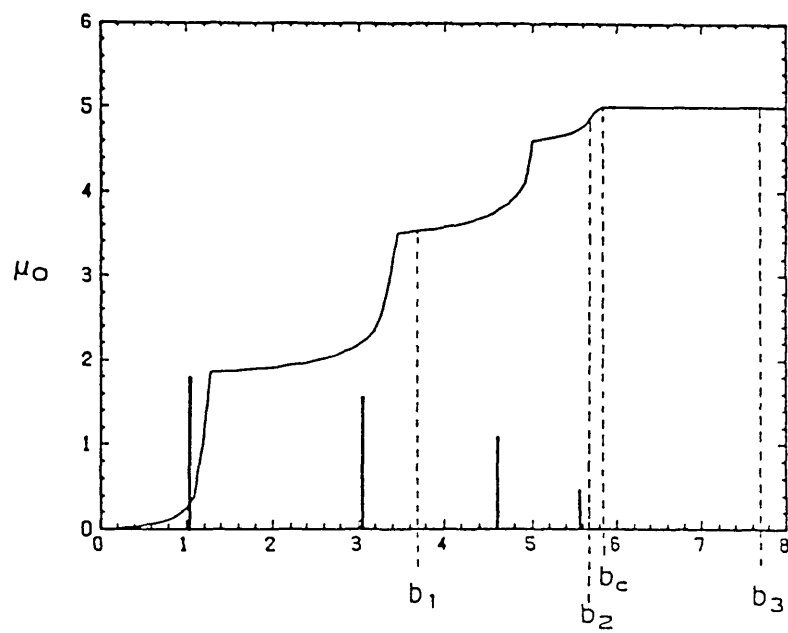


Figure 2.2.3 Weight in the rectangular band as a function of b . (Terminated fraction at 8 levels).

(2.2.5) for this value of b does not give the correct weight, μ_0 . If b is chosen such that $b > b_c$, the value at the cusp, then we recover the correct weight. The positions, ϵ_i , of the delta functions obtained by truncating the fraction at 8 levels (see (1.2.27) and (1.2.29)) are indicated in Figure 2.2.3 and their weights, w_i , shown by the heights of the lines. We are able to plot the delta functions on this graph since their positions, b_i , are given by $\epsilon_i = a \pm 2b_i$ (where $a = 0$), the positive or negative sign being used according to whether $\epsilon_i > 0$ or $\epsilon_i < 0$. As a result of the symmetry of the band, there are delta functions at $\pm\epsilon_i$ with equal weight w_i , which on this graph both lie at b_i ; for this reason the weights indicated in Figure 2.2.3 are actually $2w_i$.

In order to investigate how the loss of weight occurs we show in Figure 2.2.4 the density of states calculated with the values of $b = b_1, b_2, b_c, b_3$ shown in Figure 2.2.3. In the region outside the band we broaden any delta functions by using a small imaginary part to the energy. Within the band, $-2b \leq E \leq 2b$, we use real E . For $b = b_1$ we find two delta functions outside each band edge, corresponding to the four (because of the symmetry) ϵ_i represented in Figure 2.2.3 which are at $b_i > b$. In contrast, for $b = b_2$ there are no ϵ_i with $b_i > b$, yet the real part of the Greens function changes sign just outside each band edge, thereby giving rise to delta functions, one of which can just be seen at the upper band edge. When $b = b_c$, we obtain $\mu_0 = 5$ and the $n(E)$ shown in which there are no delta functions outside the band. At these band edges, $\pm 2b_c$, the density of states diverges. Finally, if we use a value $b = b_3$, in the region from b_c to ∞ in which $\mu_0 = 5$, then not only are tails of negligible weight pulled out from the band to the edges $\pm 2b_3$, but

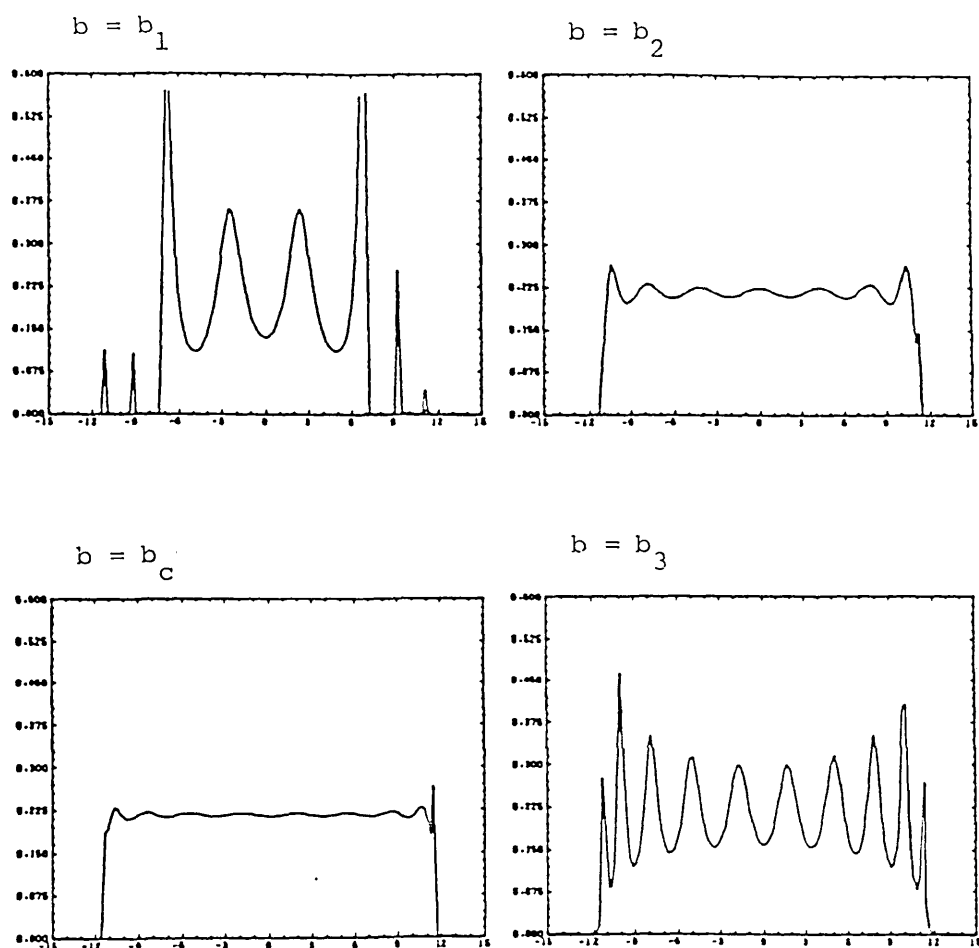


Figure 2.2.4 Densities of states for the rectangular band with various values for b . (Terminated fraction at 8 levels with $\text{Im}(E) = 10^{-4}$ outside band).

also the $n(E)$ throughout the band has developed peaks at the positions ϵ_i . For bands with internal structure, it is found that this is strongly emphasised by an overestimated bandwidth. In fact, as $b \rightarrow \infty$, the spectrum tends to a series of delta functions at the positions ϵ_i . As representations of the rectangular density of states, those obtained with $b = b_1$ and $b = b_2$ are clearly inadequate: the weight in the delta functions outside the band is not picked up by integration with $\text{Im}(E) = 0$, as seen in Figure 2.2.3. Conversely, in a real situation where we are ignorant of the bulk band edges and the form of the exact $n(E)$, any value for b chosen from the region $b_c < b < \infty$ will give the correct μ_0 .

In order to fix our choice for b we use the physically sensible criterion that we must have the minimum bandwidth, $4b$, consistent with no loss of weight from the band. Our choice, therefore, is $b = b_c$. At this value of b , the density of states at the band edges, $n(\pm 2b_c)$, diverges in such a manner that the weight in the divergence is finite. In fact, the density of states diverges at all the cusps in Figure 2.2.3. We will now show that this criterion enables us to develop a technique to find the value of $b = b_c$ for any number of a set of coefficients describing a connected band. We are interested in the value of the fraction at the band edges, $G_{00}(\pm 2b)$, where for given arbitrary b , the edges are at $\pm 2b$. Substituting for E in the terminator (2.2.4) we find that at the band edges it has the simple values

$$t(\pm 2b) = \pm b \quad (2.2.6)$$

Then, after substitution for E and some simple manipulation, the fraction is

$$G_{00}(\pm 2b) = \frac{\frac{1}{2}b_0^2}{\pm b - \frac{\frac{1}{4}b_1^2}{\pm b - \dots \frac{\frac{1}{2}b_N^2}{\pm b}}} \quad (2.2.7)$$

At the band edges, therefore, G_{00} is given by a finite fraction, and can be written as (Haydock 1980)

$$G_{00}(\pm 2b) = [(\pm b - H_S)^{-1}]_{00} = \frac{D_1(\pm b)}{D_0(\pm b)} \quad (2.2.8)$$

where $D_0(\pm b)$ is the determinant of the tridiagonal matrix

$$\pm b - H_S = \begin{vmatrix} \pm b & \frac{1}{2}b_1 & 0 & & & \\ \frac{1}{2}b_1 & \pm b & \frac{1}{2}b_2 & & & \\ 0 & \frac{1}{2}b_2 & \pm b & \dots & & \\ & & & \dots & \frac{1}{\sqrt{2}}b_N & \\ & 0 & & & \frac{1}{\sqrt{2}}b_N & \pm b \end{vmatrix} \quad (2.2.9)$$

and $D_1(\pm b)$ the determinant of $\pm b - H_S$ with the first row and column deleted. Thus, at the zeros of $D_0(\pm b)$, which are the eigenvalues of H_S , the fraction diverges at the band edges. We call these eigenvalues β_i , $i = 1, \dots, N$. Note that the eigenvalues obtained from the lower band edge, $-2b$, are simply an inversion through the origin of those for the upper band edge, $+2b$. The eigenvalues β_i are, therefore, the positions of the cusps in Figure 2.2.3, and the maximum $\beta_{\max}$ and minimum $\beta_{\min}$ ($\beta_{\max} = |\beta_{\min}|$) give the position of

the first cusp at b_c , where $\mu_0 = 5$. This is the choice of b we must make so as to satisfy the criterion of minimum bandwidth with no loss of weight from the band.

In summary, we have found for the rectangular band that by investigating the value of the fraction at the band edges for a given b , we can construct a finite tridiagonal matrix whose eigenvalues, β_i , are the values of b for which the fraction diverges at the upper and lower band edges. Choosing b to be the maximum, $\beta_{\max}$, or the modulus of the minimum, $|\beta_{\min}|$, gives us the b_c that satisfies our physical criterion.

Clearly, the value of b_c obtained in this fashion will depend on the number of levels used in the fraction. We show the terminating parameter b_c determined by this procedure for i levels together with the coefficients b_i in Figure 2.2.5. With increasing number of levels b_c tends to b_∞ , which in this case is known from the bandwidth; for only a few levels there are considerable variations from the asymptotic value. This is in the nature of the technique: the constant tail added to the fraction is not necessarily a close approximation for a small number of levels to the asymptotic behaviour of the coefficients but is such as to assure the satisfaction of the bandwidth criterion.

2.2.3 Magnitude Matching and the Skew Rectangular Band

The skew rectangular band (Figure 1.2.4) lacks the inversion symmetry of the simple rectangular band; therefore its $a_i \neq 0$ (Figure 2.2.1) and the terminating parameter a will not vanish in general. This ensures that our continued development here is valid for the

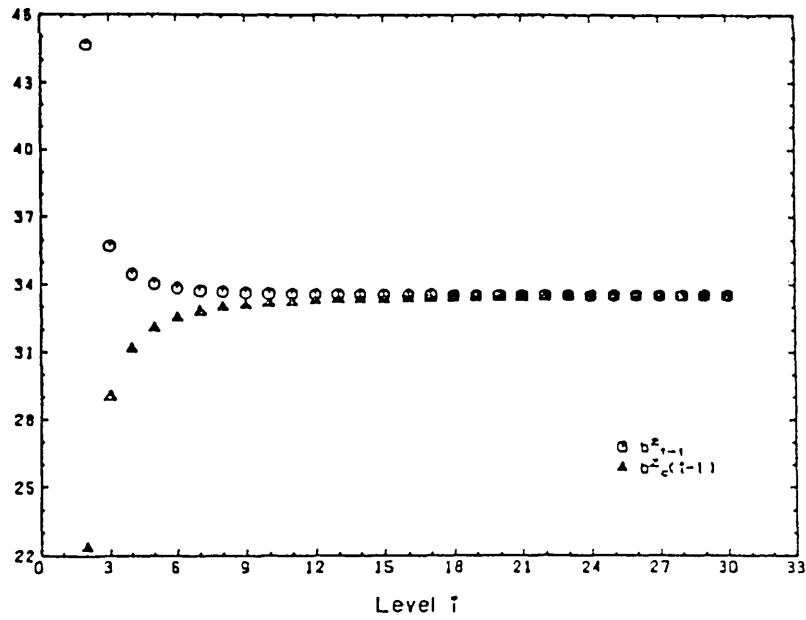


Figure 2.2.5 The rectangular band coefficients, b_{i-1}^2 , and the calculated terminating coefficient, $b_c^2(i)$.

general case. The band edges are now given by $a \pm 2b$, but we still find that the terminator at these edges has the simple values

$$t(a \pm 2b) = \pm b \quad (2.2.10)$$

The Greens function at the edges is now given by the finite terminated fraction:

$$G_{00}(a \pm 2b) = \frac{\frac{1}{2}b_0^2}{\pm b - \frac{1}{2}(a_0 - a) - \frac{\frac{1}{4}b_1^2}{\pm b - \frac{1}{2}(a_1 - a)} \dots \frac{\frac{1}{2}b_N^2}{\pm b - (a_N - a)}} \quad (2.2.11)$$

which can be written

$$G_{00}(a \pm 2b) = [(\pm b - H_S(a))^{-1}]_{00} \quad (2.2.12)$$

Diagonalisation of the matrix

$$H_S(a) = \begin{pmatrix} \frac{1}{2}(a_0 - a) & \frac{1}{2}b_1 & 0 & & 0 \\ \frac{1}{2}b_1 & \frac{1}{2}(a_1 - a) & \frac{1}{2}b_2 & & \\ 0 & \frac{1}{2}b_2 & \frac{1}{2}(a_2 - a) & \dots & \\ & 0 & & \dots & \frac{1}{\sqrt{2}}b_N \\ & & & \frac{1}{\sqrt{2}}b_N & (a_N - a) \end{pmatrix}$$

yields the eigenvalues β_i , $i = 1, \dots, N$ which are implicit functions of a and which do not have inversion symmetry through the origin. The eigenvalues obtained for the lower band edge are, however, still an inversion of those obtained for the upper band edge.

For given a , the eigenvalues β_i obtained for the upper band

edge are those values of b for which $G_{00}(a + 2b)$ diverges, and the eigenvalues obtained from the lower band edge are those values of $-b$ for which $G_{00}(a - 2b)$ diverges. Thus the b_c for the upper band edge ($b_c = \beta_{\max}$) is different in general from the b_c for the lower band edge ($b_c = |\beta_{\min}|$). Although it was not made explicit in the development for the rectangular band, the minimum bandwidth for no loss of weight occurs when the fraction diverges simultaneously at both band edges. This corresponds to a delta function being about to separate simultaneously from both edges. We achieve this condition by varying the parameter a in $H_S(a)$ until

$$\beta_{\max} = |\beta_{\min}| = b_c \quad (2.2.14)$$

which occurs at $a = a_c$.

We can confirm that these parameters a_c , b_c satisfy the bandwidth criterion by investigating the weight in the band, μ_0 , as a function of the terminating parameters a , b in the region near a_c , b_c . The full line in Figure 2.2.6 for $a = a_c$ shows that $\mu_0 = 5$ at $b = b_c$ as expected. For $a \neq a_c$, however, we find that the weight behaves as the broken line. The two values b_1 , b_2 correspond to divergence at the upper and lower band edges, which now occur at different values for the bandwidth. We plot in Figure 2.2.7 the locus in the a , b plane of the cusp where μ_0 is just equal to 5. Above and on the full line $\mu_0 = 5$ and below it $\mu_0 < 5$. The dotted continuations correspond to the cusp at b_1 in Figure 2.2.6. The minimum bandwidth, $4b_c$, giving $\mu_0 = 5$ occurs precisely at a_c .

The simple procedure developed in this and the preceding section has been coded as FORTRAN subroutines using standard library routines for the diagonalisation of $H_S(a)$ (equation (2.2.13)) and the location

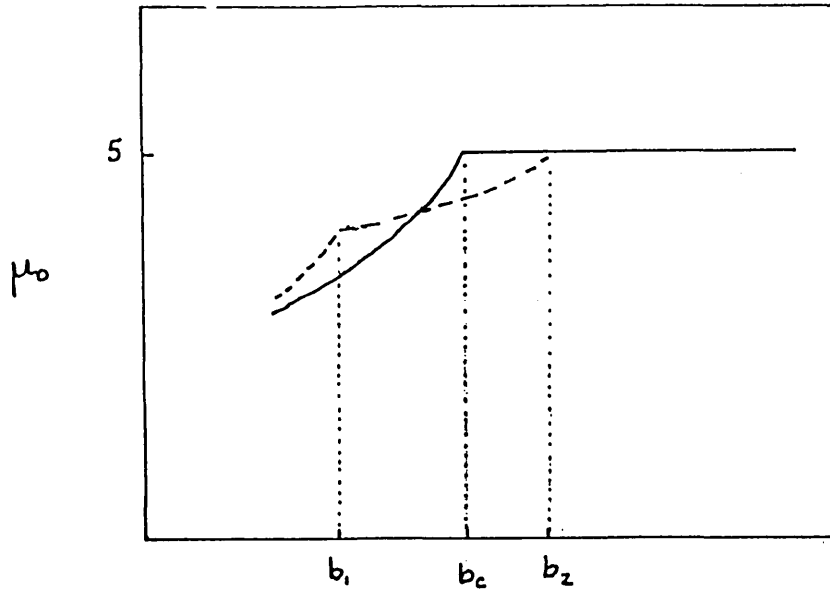


Figure 2.2.6 Weight in the skew rectangular band as a function of b for:

$a = a_c$ (full line)

$a \neq a_c$ (broken line)

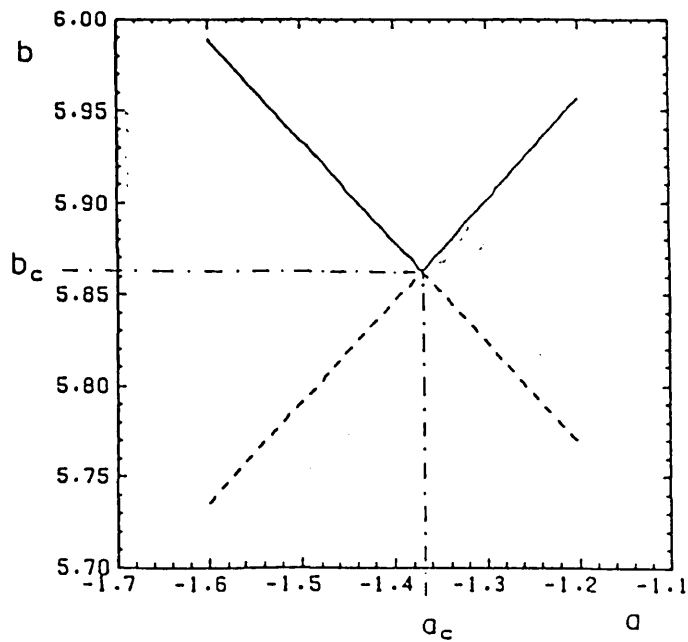


Figure 2.2.7

The locus of the $\mu_0 = 5$ cusp in the a, b plane for the skew rectangular band. (Terminated fraction at 8 levels).

of the zero of $B(a) = \beta_{\max} - |\beta_{\min}|$ (equation (2.2.14)). They are listed in the Appendix and copies are available from the author on request. The operation of the computer routines for the determination of a_c , b_c is entirely automatic and requires no input other than the set of coefficients a_i , b_i , $i = 1, \dots, N$ and the number of levels for which the terminating coefficients are desired.

In Figure 2.2.8 we show the skew rectangular band coefficients, a_i , b_i^2 , and the terminating parameters, $a_c(i)$, $b_c^2(i)$, determined as described above. These parameters exhibit rapid convergence towards the asymptotic limits. The density of states calculated with the a_c , b_c are shown in Figure 2.2.9 for various numbers of levels. The necessary divergence of $n(E)$ at the band edges distorts the spectrum obtained, but this distortion decreases with more levels. These graphs should be compared with those in Figure 2.1.3 where the density of states is calculated with the Cambridge method. We see that the convergence towards the exact $n(E)$ is similar in both methods, although for few levels the termination technique produces, perhaps, a better representation of the $n(E)$ than does the Cambridge method.

The convergence of the structural energy, $U(N)$, given by equations (2.1.7) and (2.1.8) is shown in Figure 2.2.10. The $U(N)$ is shown relative to the exact $U(N)$ (equations (2.1.13) and (2.1.14)). Comparison with the structural energies and their error bounds calculated with the Cambridge method (Figures 2.1.8 and 2.1.9) shows that the terminated $U(N)$ converge considerably faster. Moreover, counting of the zeros in the $U(N)$ for n levels relative to the exact reveals that the condition of $2n - 2$ zeros derived from the moment theorem (Ducastelle and Cyrot-Lackmann 1971) is always satisfied, in striking contrast to the situation found for calculation with the

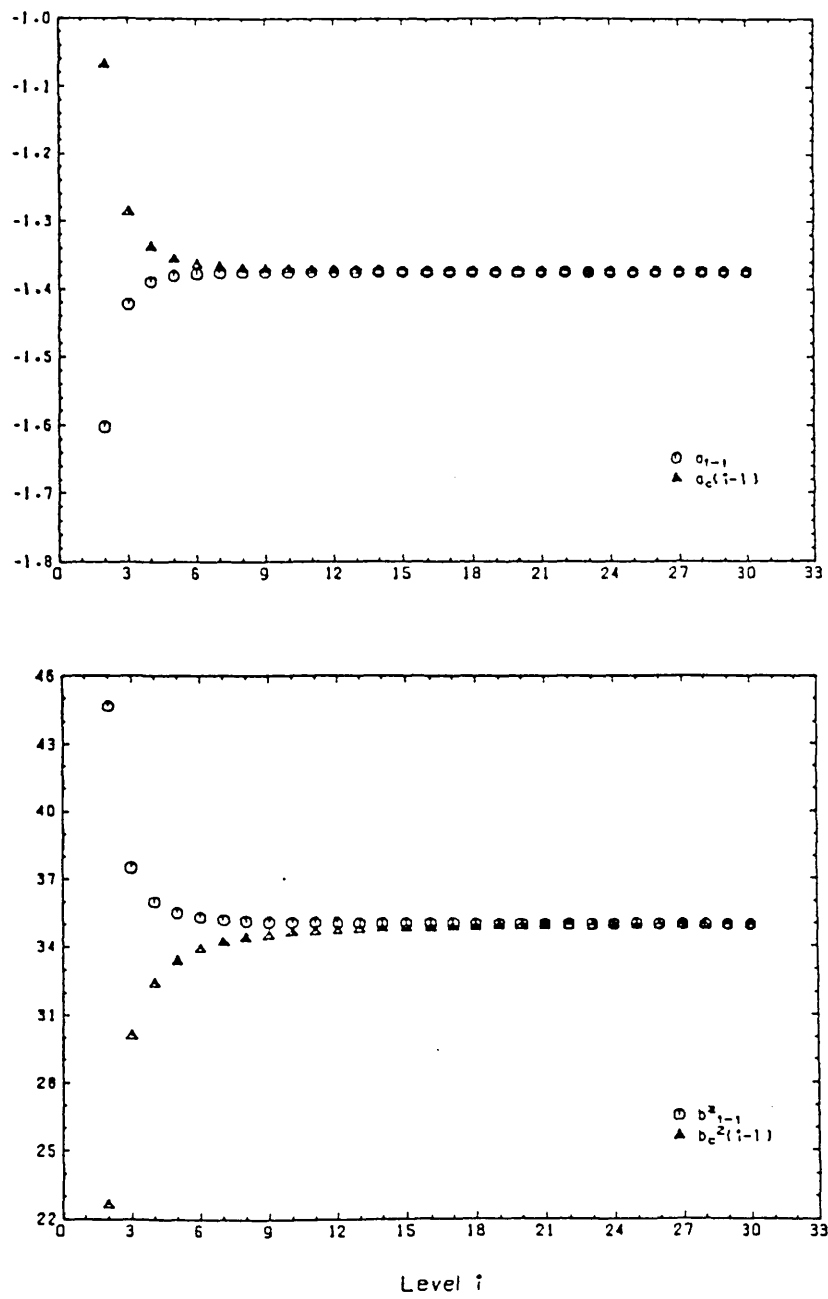


Figure 2.2.3 The skew rectangular band coefficients and terminating parameters, a_c , b_c^2 .

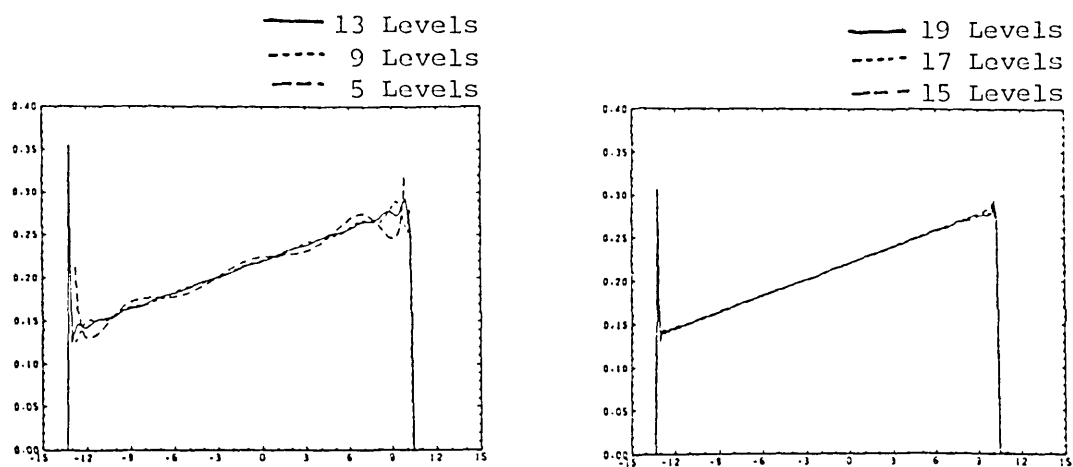


Figure 2.2.9 The convergence of the terminated approximation to the skew rectangular density of states.

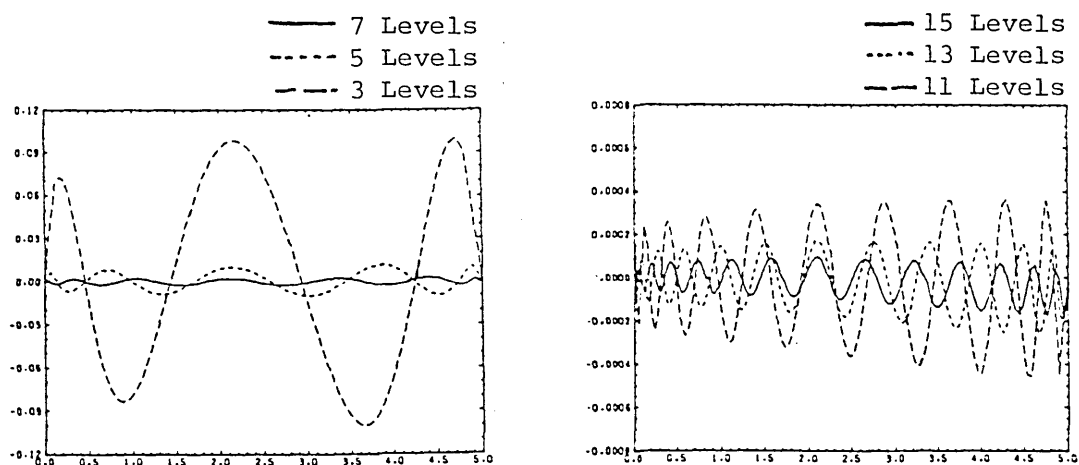


Figure 2.2.10 The structural energy of the skew rectangular band relative to the exact energy. (Termination technique).

Cambridge method.

2.2.4 FCC

We now present the results of the application of our termination method to the coefficients describing the canonical FCC band. Although the edges of this band are known to be (Pettifor 1977)

$$E_b = -16.4 \quad E_t = 10.9 \quad (2.2.15)$$

the calculation here uses only first nearest neighbour hopping and the coefficients, therefore, do not tend to the asymptotic limits derived from (2.2.15), as can be deduced from Figure 2.2.2. The convergence of the coefficients is too slow to allow accurate estimation of the asymptotic limits. The canonical FCC band, then, provides a test of the applicability of the technique in a "real" situation. In addition, the results presented here will be used in a later Chapter concerned with the transition metal structures. The FCC coefficients used are the "average" coefficients calculated as described in 1.2.4, of which the first 20 pairs are exact, the last 9 being approximate due to cluster boundary effects.

Figure 2.2.11 shows the $n(E)$ obtained using our termination technique for various numbers of levels. These are compared with the band-structure calculation of R. Muniz (private communication) and this Figure should be compared with Figure 2.1.4 showing the $n(E)$ obtained with the Cambridge method. By 7 levels the $n(E)$ obtained is a good representation of the bulk, with the four major peaks well resolved. There are visible divergences at the band edges but these become

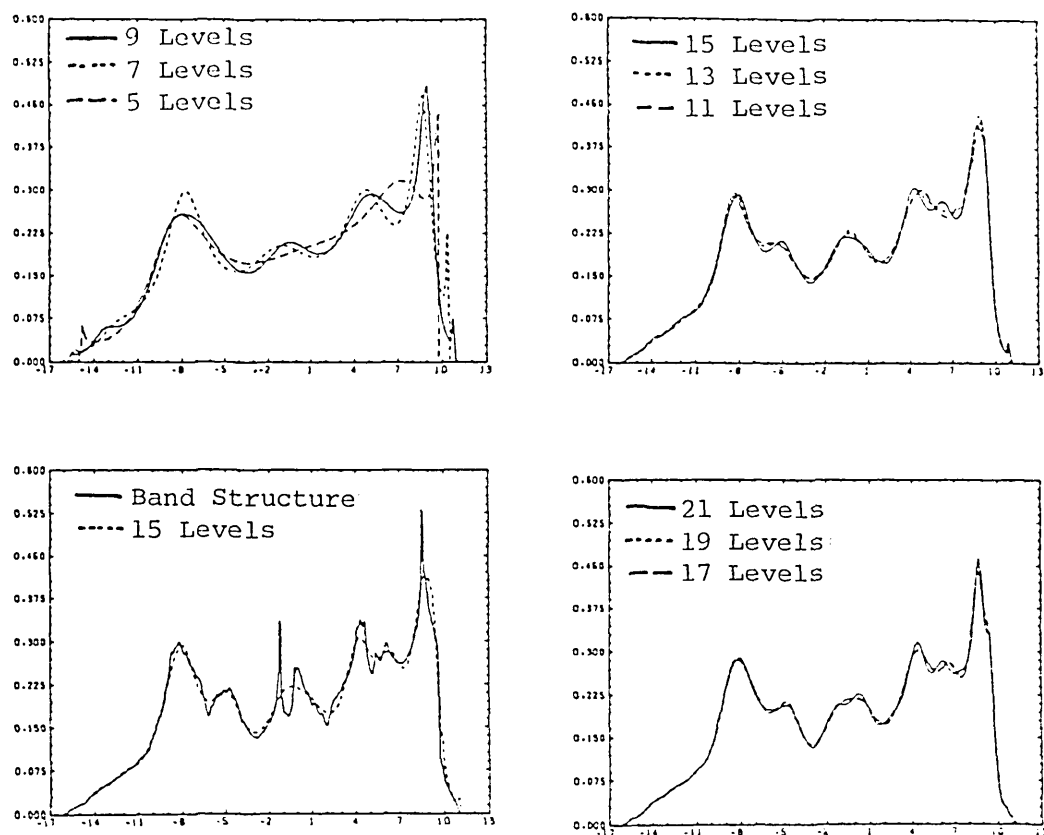


Figure 2.2.11 Convergence of the terminated approximation to the FCC density of states.

negligible with further levels. At 15 levels the comparison between the exact and reconstructed $n(E)$ is very good. The twin peak structures at $E \approx 6$ and $E \approx -7$ have been resolved (note in Figure 2.1.4 that this is not done by the Cambridge method). We find that for the fine structure at $E \approx 0$ it is necessary to use about 20 levels. Neither the terminated nor the Cambridge method, of course, can hope to reproduce the internal singularities in the band with such numbers of levels because these are long range effects. The termination technique, though, gives a better representation of the $n(E)$ and, although the details of the spectrum are not reproduced until many levels are included, they are superior to those produced by the Cambridge method.

More importantly, and as expected from the results for the rectangular and skew rectangular bands, we find (Figure 2.2.12 and compare Figure 2.1.10) that the structural energy is extremely quickly convergent. By 5 levels the structure of $\Delta U(N)$ is established, further levels changing the positions of the zeros only slightly. For more than 11 levels the $\Delta U(N)$ are indistinguishable on this scale. Note that the $\Delta U(N)$ exhibit the correct number of zeros, indicating that for the FCC band, as well as for the model bands considered earlier, the moments are preserved in the calculation of the density of states and integrated quantities.

With reference to 2.1.3, we can simply explain the reason why the termination technique preserves the moments. The terminator $t(E)$ in (2.2.2) has the form of a continued fraction (2.1.22) by definition. Thus, provided that the bandwidth, $4b$, is sufficient that no weight is lost from the band, the correspondence between the power series expansion of the terminated fraction and the true fraction (2.1.23) holds and the coefficients in the terminator, whatever their value,

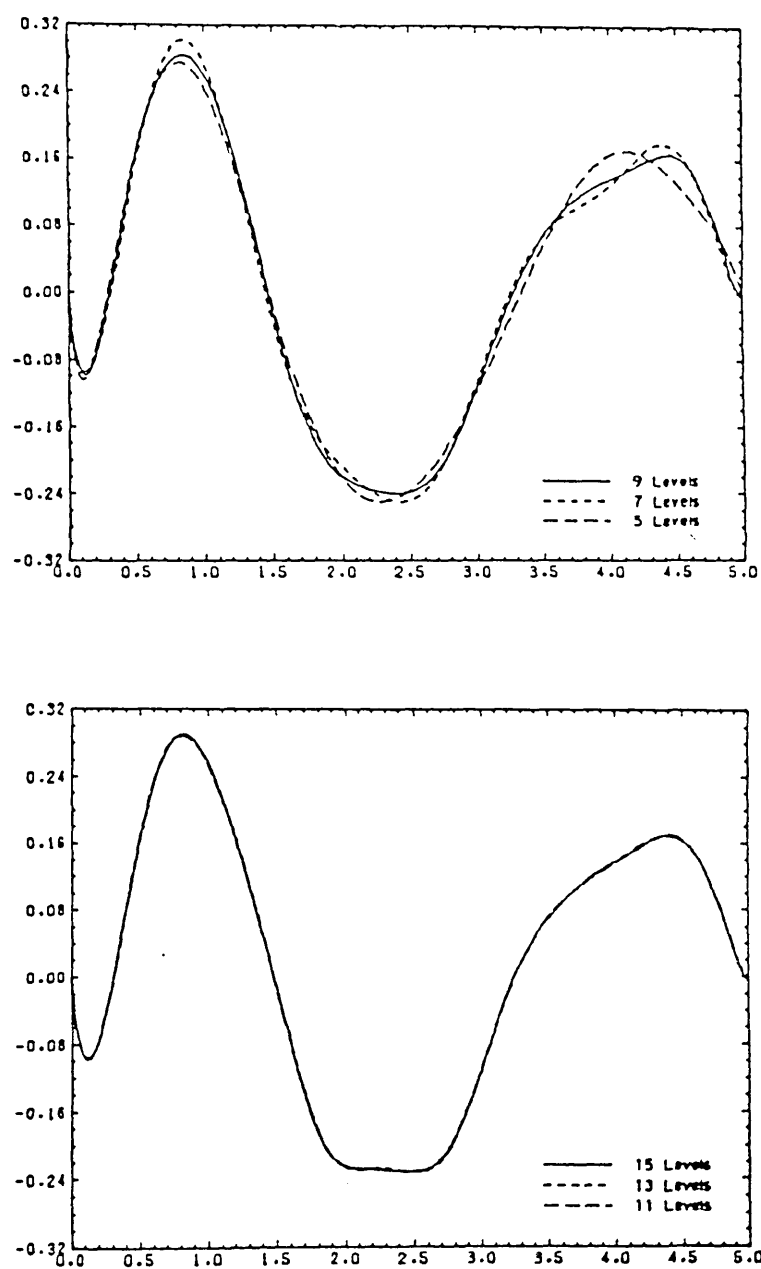


Figure 2.2.12

The structural energy of the FCC band relative to the exact skew rectangular energy. (Termination technique).

contribute only to the terms of order E^{2n+1} and greater, leaving the moments μ_i $i \leq n$ equal to their true values.

For the example bands used in this and the preceding sections we have, in fact, known the true band edges, from which we can derive the asymptotic limits of the coefficients. In Figure 2.2.13 we show the skew rectangular band calculated with the asymptotic values a_∞ , b_∞ in the terminator. We see that, of course, the density of states no longer diverges at the band edges although there are still oscillations near the edges. If we calculate the $U(N)$ with the asymptotic terminator we find that the structural energy relative to the exact has the same form as in Figure 2.2.10 but it is smaller by about an order of magnitude. This is a slightly artificial example since the coefficients are so rapidly convergent (Figure 2.2.1); by 9 levels we are essentially in the asymptotic region. The FCC coefficients shown in Figure 2.2.2 are less rapidly convergent. Although their limits are not the asymptotic values derived from (2.2.15), these should be a reasonable approximation for the asymptotic terminator. In Figure 2.2.14 we show the densities of states and in Figure 2.2.15 the structural energy, $\Delta U(N)$, calculated with the asymptotic terminator. Apart from the absence of the divergence at the band edges, there is really little difference between these quantities and those shown in Figures 2.2.11 and 2.2.12 calculated with the new termination technique.

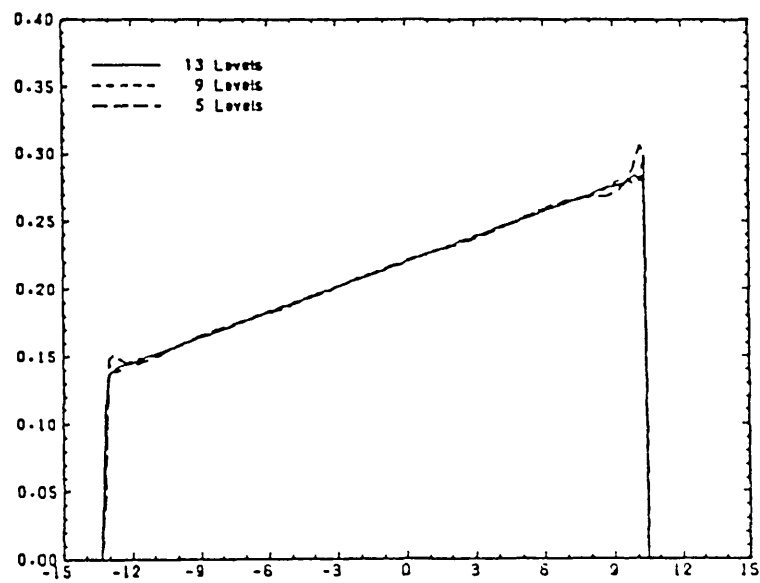


Figure 2.2.13 Convergence of the terminated approximation to the skew rectangular density of states using the asymptotic terminator.

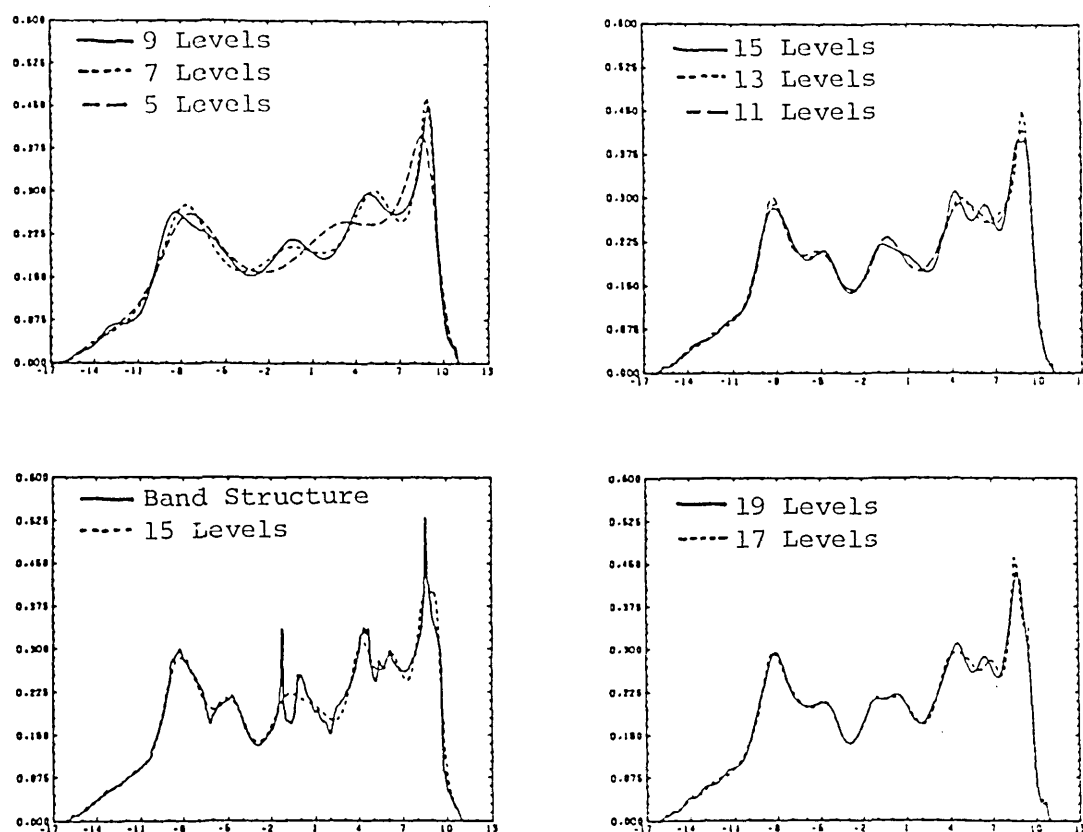


Figure 2.2.14

Convergence of the terminated approximation to the FCC band using the asymptotic terminator.

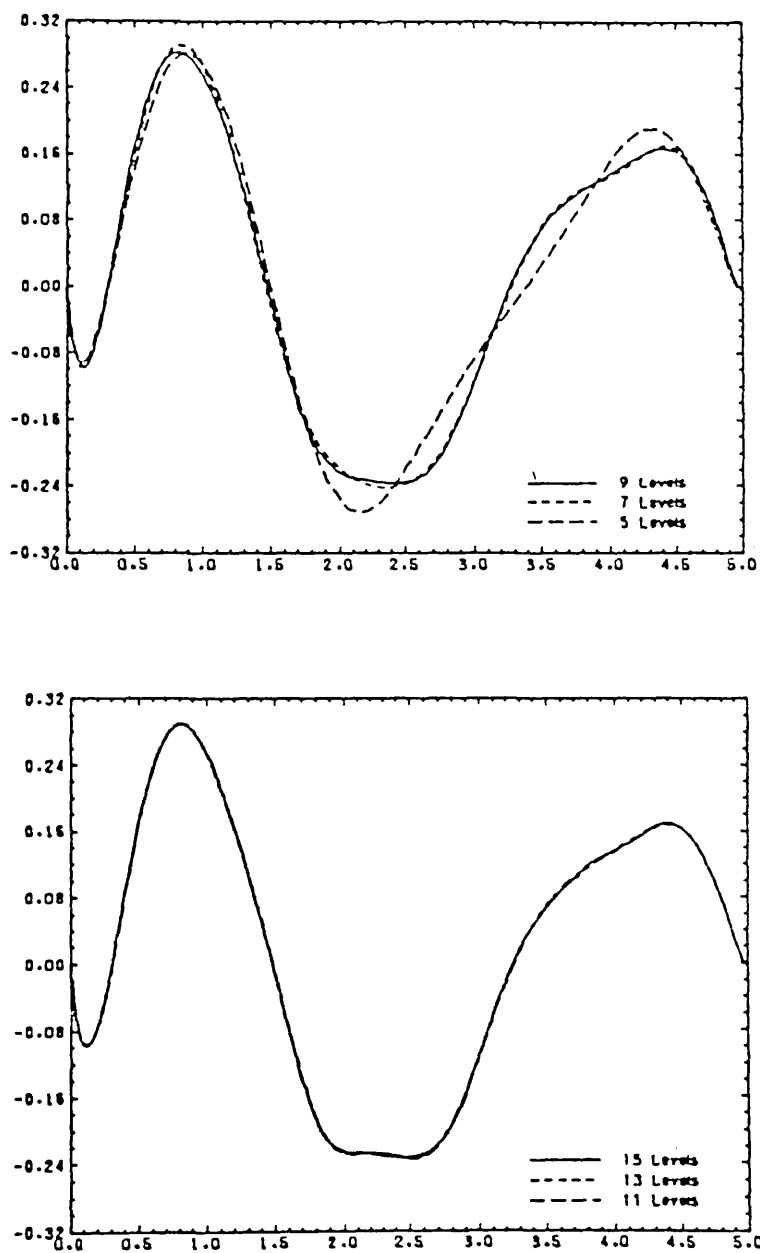


Figure 2.2.15 The structural energy of the FCC band relative to the exact skew rectangular energy using the asymptotic terminator.

§2.3 Cluster Size and the Length of the Continued Fraction

In the preceding sections, the coefficients used in the calculations of $n(E)$ and $U(N)$ by the termination method have all been exact. For coefficients derived from cluster calculations with the recursion method, the cost of obtaining more than about 5 - 8 exact coefficients may well be considered prohibitive. For this reason, most, if not all published applications of the recursion method have used many inexact coefficients. The Cambridge method relies on using inexact coefficients (Haydock 1980) in the sense that convergence of the $n(E)$ is not achieved until about 1.5 to 2 times the number of exact levels. It has, however, been seen that this stable form may still not be a very good representation of the true $n(E)$.

Similar studies have not been published for the terminated fraction. In this section we study, therefore, the effect of inexact coefficients on the density of states and related integral quantities calculated with the termination technique. We derive a general "rule of thumb" for determining the length of the continued fraction to be used for a given cluster size.

2.3.1 Projection of the Recursion Orbitals onto the Real Lattice

We begin by investigating the behaviour of the recursion orbitals and the effect of the cluster boundary on them.

The recursion orbital $|\phi_n\rangle$ is a linear combination of tight binding basis orbital $|\psi_m\rangle$ (Haydock et al 1975). We deal, for simplicity, with orbitals of one irreducible representation of the

point group of the lattice, for example t_{2g} or e_g , or with the "average" orbital. The orbital $|\phi_n\rangle$ may therefore be written

$$|\phi_n\rangle = \sum_m c_{nm} |\psi_m\rangle \quad (2.3.1)$$

where the sum is over all tight binding orbitals in the cluster. With the neglect of overlap, we may project out the weight of $|\phi_n\rangle$ on a particular orbital $|\psi_j\rangle$:

$$\langle \psi_j | \phi_n \rangle = c_{nj} \quad (2.3.2)$$

We define the R th "hopping shell" to be those orbitals that can be reached by $R - 1$ direct nearest neighbour hops from the central orbital $|\psi_0\rangle$ (i.e. they cannot be reached in $R - 2$ hops). This implies that the central orbital is in hopping shell 1. By projecting out the weight of $|\phi_n\rangle$ onto each orbital $|\psi_j^R\rangle$ in the R th hopping shell, summing over j and normalising with $\langle \phi_n | \phi_n \rangle$ we obtain the proportion of the weight of $|\phi_n\rangle$ that is localised on the tight binding orbitals of the R th hopping shell:

$$w_{nR} = \sum_j \frac{|\langle \psi_j^R | \phi_n \rangle|^2}{\langle \phi_n | \phi_n \rangle} = \frac{\sum_j c_{nj}^2}{\sum_m c_{nm}^2} \quad (2.3.3)$$

Thus $\sum_R w_{nR} = 1$. We also define a measure, R_n , of the radial extent of $|\phi_n\rangle$ by

$$R_n^2 = \sum_R R^2 w_{nR} \quad (2.3.4)$$

R_n is thus the root mean square extent of the orbital. Hodges et al (1980) have used a similar quantity to investigate the behaviour of the recursion orbitals in disordered solids.

Four sets of coefficients for FCC clusters have been used in this investigation. Each set consists of 29 pairs of coefficients calculated from clusters consisting of, respectively, only 5, 10, 15 and 20 hopping shells. They are shown in Figure 2.3.1. In these coefficients, then, 5, 10, 15 and 20 pairs will be exact. The shape of the clusters has been chosen so as to minimise the number of atoms required for a given number of exact levels: if R exact pairs of coefficients are desired, we include only those atoms in the hopping shells up to and including the R th (because the atoms in the $R + 1$ th shell only contribute to levels $N > R + 1$). Some discussion of cluster shape will be given later in this section.

In Figure 2.3.2 we show the behaviour of R_n , the r.m.s. extent of the recursion orbitals, as a function of the number of levels, n , for each of the four sets of coefficients. In the region where the coefficients are exact, R_n is approximately proportional to n , but once the levels become inexact R_n tends towards an approximately constant value which is about 0.65 - 0.7 times the number of exact shells. This behaviour is simply due to the requirement that, for all n , all the weight of $|\phi_n\rangle$ must be contained within the cluster. Thus the value of R_n could never exceed the number of hopping shells in the cluster and could only equal it if all the weight of $|\phi_n\rangle$ were localised on the boundary. Table 2.3.1 shows the deviations from the exact R_n for various numbers of levels. The deviations are proportionally smaller for the larger clusters, and the same can be seen in Figure 2.3.1 to be the case for the deviations of the

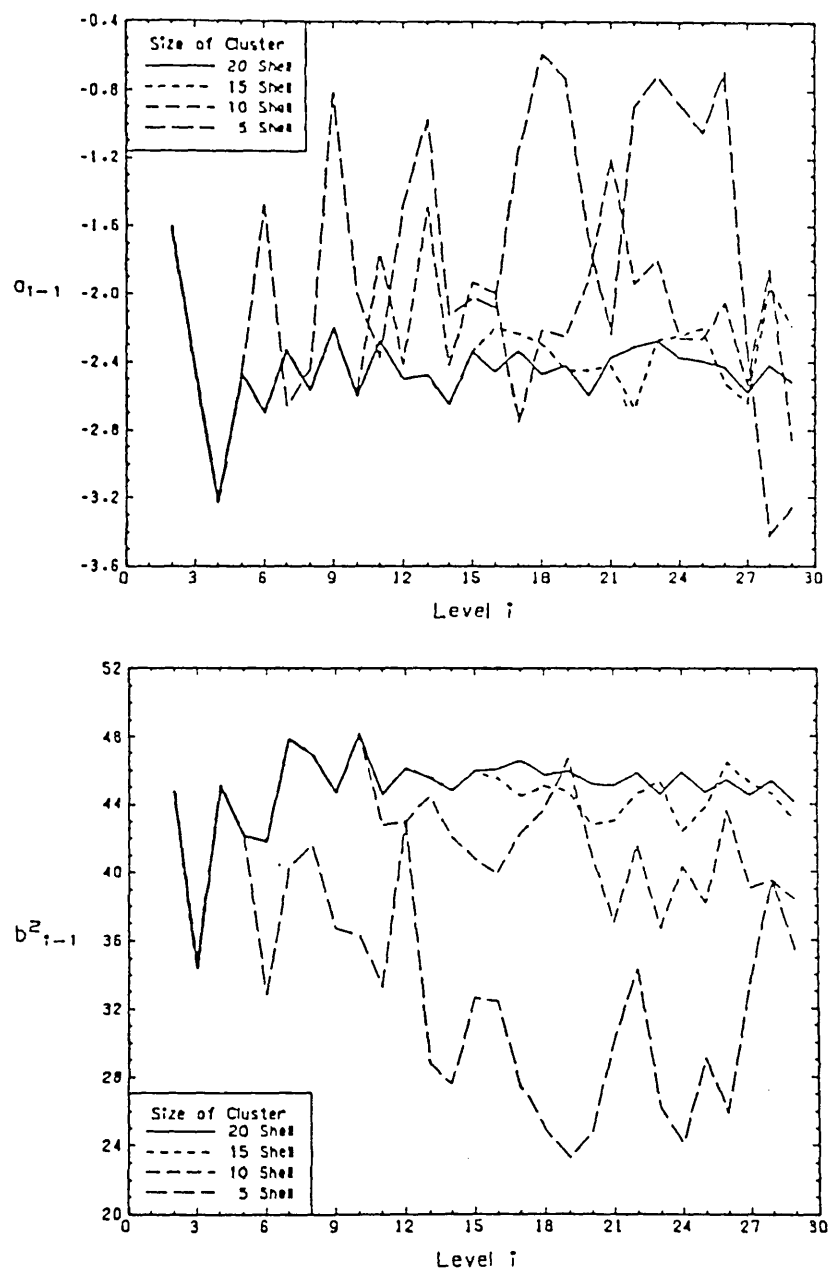


Figure 2.3.1 Effect of cluster size on the FCC average coefficients

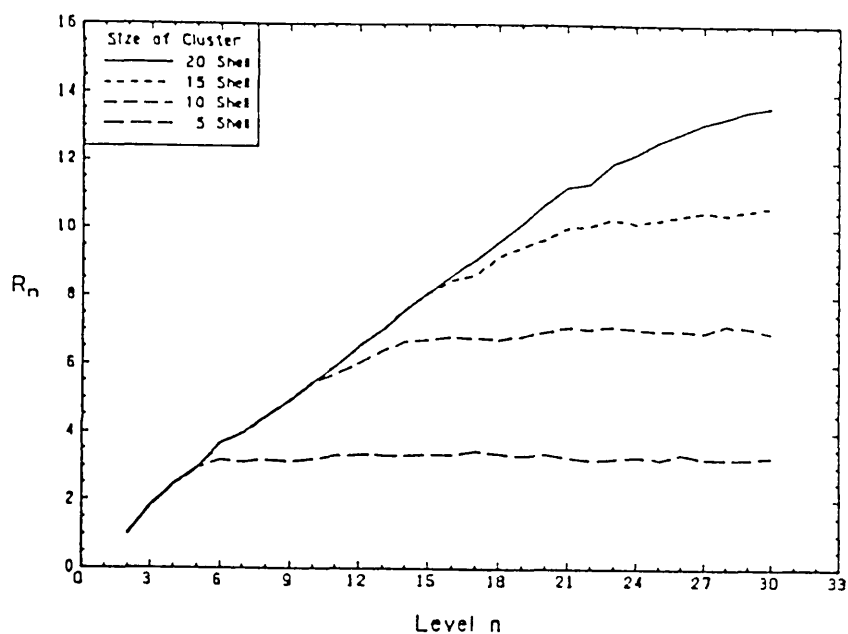


Figure 2.3.2 R.M.S. extent of the recursion orbitals, R_n , for various FCC cluster sizes.

5 Level Cluster		10 Level Cluster		15 Level Cluster	
N ^o . of levels	Deviation %	N ^o . of levels	Deviation %	N ^o . of levels	Deviation %
6	-13.1	11	-7.2	16	-1.2
7	-20.5	12	-7.7	17	-4.7
		13	-8.6	18	-4.7
		14	-11.8	19	-6.5
				20	-9.3
				21	-10.7*

*base is approximate R_n calculated from 20 level cluster. This is thought to be less than 1% different from the exact.

Table 2.3.1 Deviation of R_n from the exact value.

coefficients from the exact values.

We can obtain further detail of the behaviour of the recursion orbitals by investigating how the distribution through the cluster of the weight of $|\phi_n\rangle$ changes with the number of levels and with the size of the cluster. We thus consider the weight w_{nR} (equation 2.3.3) as a function of R . In Figure 2.3.3(a) we show the distribution of w_{nR} in the 10 shell cluster for a number of levels greater than the exact; in these we should be able to detect the effect of the boundary. For comparison, in Figure 2.3.3(b) we have constructed for the 20 shell cluster new weights w'_{nR} which are the proportions of the weight on the shell R out of a total weight which is the weight contained within the 10 shells:

$$\begin{aligned}
 W_n &= \sum_{R=0}^9 w_{nR} & (W_n < 1 \text{ for } n > 10) \\
 w'_{nR} &= \frac{w_{nR}}{W_n}
 \end{aligned}
 \tag{2.3.5}$$

Thus for Figure 2.3.3(b) the "boundary" around the hopping shells 1 - 10 is penetrable; some of the weight of $|\phi_n\rangle$ can move beyond it and we normalise the distribution within the boundary by whatever total weight is left within. On the other hand, for Figure 2.3.3(a) the boundary is impenetrable; no weight can move beyond it. Use of this device allows a realistic discussion of the effects of the boundary.

We see that, in general, even for many levels relative to the number of exact, the form of the distribution within 10 shells is broadly similar. For the 10 level cluster the distribution is skewed slightly towards the more distant shells. This is confirmed if we compare (Table 2.3.2) the R_n for the 10 shell cluster with the new

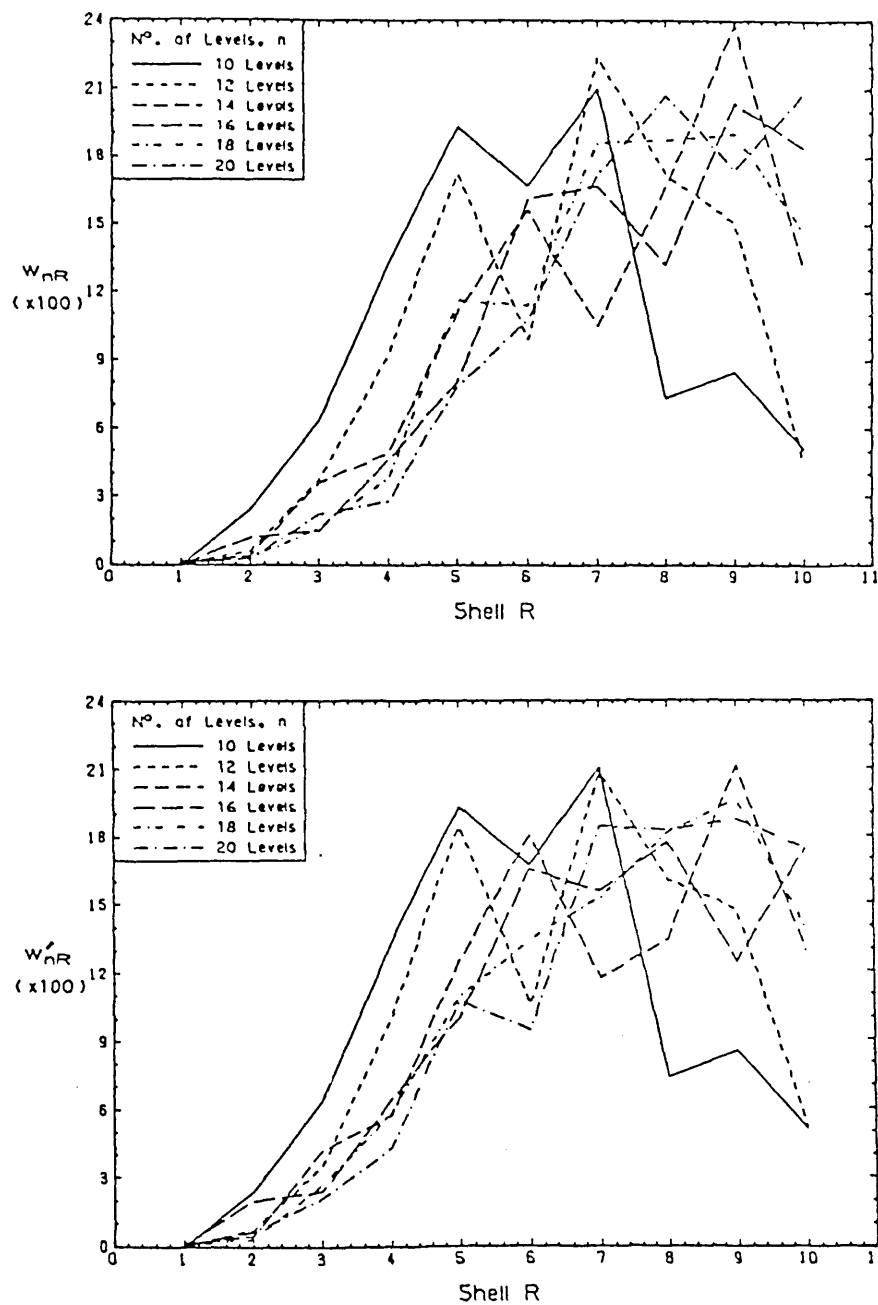


Figure 2.3.3

Distribution of weight of recursion orbitals over the hopping shells in FCC clusters.
 (a) 10 shell cluster
 (b) 10 shells of 20 shell cluster.

Level n	R'_n	R_n
10	5.43	5.43
12	5.96	6.01
14	6.47	6.65
16	6.53	6.80
18	6.62	6.72
20	6.79	6.97

Table 2.3.2 R.M.S. extent of orbitals for 10 shell cluster (R_n from (2.3.4)) and 10 shells of 20 shell cluster (R'_n from (2.3.6))

R'_n for the 20 shell cluster defined by

$$(R'_n)^2 = \sum_{R=0}^9 R^2 w'_{nR} \quad (2.3.6)$$

where the w'_{nR} are given by (2.3.5).

The reason for the accumulation of weight near the boundary is simply explained. Consider a path consisting of 10 nearest neighbour hops which thus contributes to the orbital for 11 levels. When the boundary is penetrable (i.e. in the 20 shell cluster) this path can extend out to shell 11, passing through shell 10 at hop 9. Part of its weight is therefore located outside the boundary. In the 10 shell cluster, however, once this path has reached shell 10 it can only stay within this shell or hop back to shell 9. Those paths that would continue beyond the boundary if the orbitals were available are "folded back" into the cluster and will, at least initially, tend to remain in the shells close to the boundary. This confining effect of the impenetrable boundary is the reason for the skewing in the distribution of weight.

It should, perhaps, be noted that this device of inserting a penetrable boundary around 10 shells in the full size cluster of 20 shells is not precisely equivalent to a cluster of only 10 shells with free boundary conditions - i.e. that if a path hops out of the cluster from the 10th shell, then it is entirely lost and makes no contribution within the 10 shells. The reason for the difference is that there are a small number of paths of length $n > 10$ which make a contribution to the weight on one of the shells $R \leq 10$ by hopping through the boundary to the 11th shell and then later hopping back to the 10th, and then possibly to shells $R \leq 10$.

2.3.2 Effects of the Boundary on the Density of States and the Energy

In 2.3.1 we characterised the effect of the cluster boundary in terms of the distribution of weight and the r.m.s. extent of the recursion orbitals, and showed the effect on the FCC coefficients. We now use those coefficients to demonstrate the effect of the boundary on the quantities of interest; the density of states and the structural energy. Figure 2.3.4 shows the density of states calculated for various numbers of levels with the coefficients obtained from the 10 shell cluster. Of the levels used, therefore, only 10 are exact. With 11 levels the $n(E)$ is still relatively similar to that in Figure 2.2.11 with all levels exact, although there is some emphasis of the internal features. This emphasis of the features of the density of states is so pronounced in the $n(E)$ for 13 and 15 levels that these cannot be considered nearly as good representations of the FCC $n(E)$ as those in Figure 2.2.11. Further levels simply increase the tendency towards a delta function spectrum.

The boundary has, therefore, a dramatic effect on the density of states at the central atom. Notice that for these numbers of levels, the $n(E)$ obtained with the Cambridge method are still tending towards a stable form (Figure 2.1.4). Haydock and co-workers (Haydock 1980; Kelly 1980; Haydock et al 1975) argue that for only a few levels beyond the exact the boundary effects are small because the largest contribution to the coefficients comes from paths that wind around close to the central atom and which are, therefore, unaware of the boundary. This, they feel, is the reason why the Cambridge method gives densities of states that continue to converge towards a stable form for between 1.5 to 5 times the number of exact levels. The

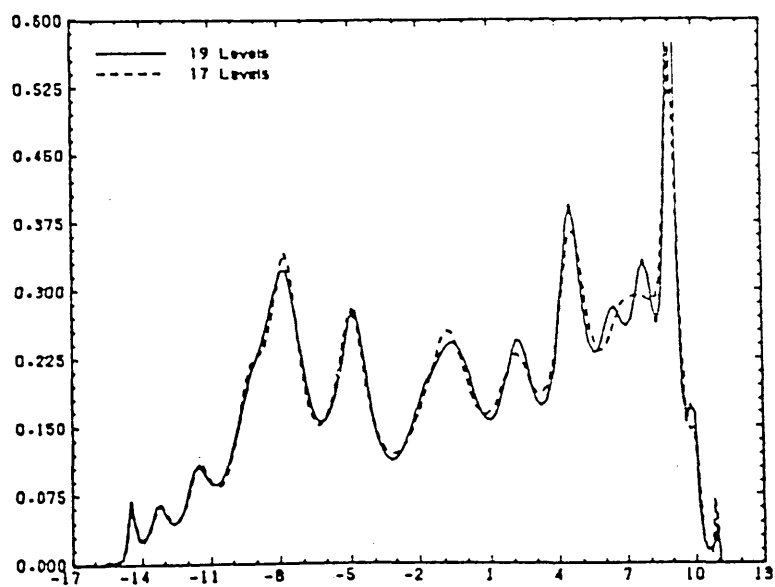
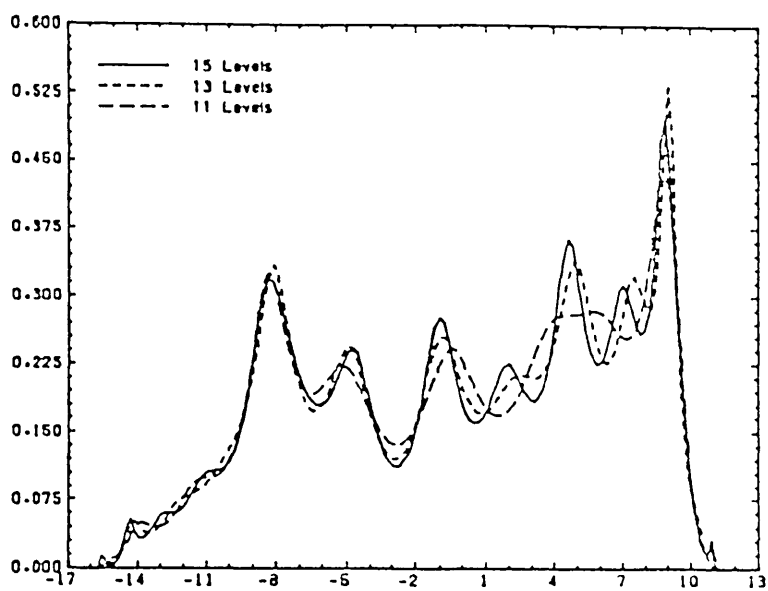


Figure 2.3.4

Canonical FCC density of states for various numbers of levels, of which 10 are exact. (Termination technique)

effects on the coefficients shown in Figure 2.3.1, the r.m.s. extent in Figure 2.3.2 and the $n(E)$ in Figure 2.3.4 contradict their argument. We find from Figure 2.3.2 that the r.m.s. extent of, for example, the 13th level is 6.3 in the 10 shell cluster when it would be 7.0 if the cluster were infinite. This is due to 12% of the weight of this orbital in the infinite cluster being beyond the 10th shell. When the impenetrable boundary is imposed, not only are the paths out of the 10th shell denied to the procedure, but also this 12% must be incorporated into the weight in the outer shells of the finite cluster. This is hardly a small effect.

The results produced here seem to indicate that the delay in the convergence of the Cambridge method until about 1.5 to 5 times the exact levels is not due to the boundary effects being negligible but is rather a consequence of its manner of reconstruction of the density of states. We believe that the "over-smoothing" produced by the Cambridge method obscures the boundary effects and leads to the apparent reliance on inexact levels. In contrast, the termination technique responds immediately to the effects in the coefficients produced by the boundary.

With reference to Figure 2.3.5, we find that $\Delta U(N)$, the structural energy relative to the exact skew rectangular energy, is relatively unaffected by the boundary. The inexact levels introduce spurious oscillations about the exact value for $\Delta U(N)$. A recent calculation by Finnis et al (private communication and 1983) of the band structure contribution to the C_{44} elastic constant of vanadium has confirmed this result. The relatively small effect that the boundary has on the energy for a few levels beyond the exact accords with the superior convergence of the energy found in the previous

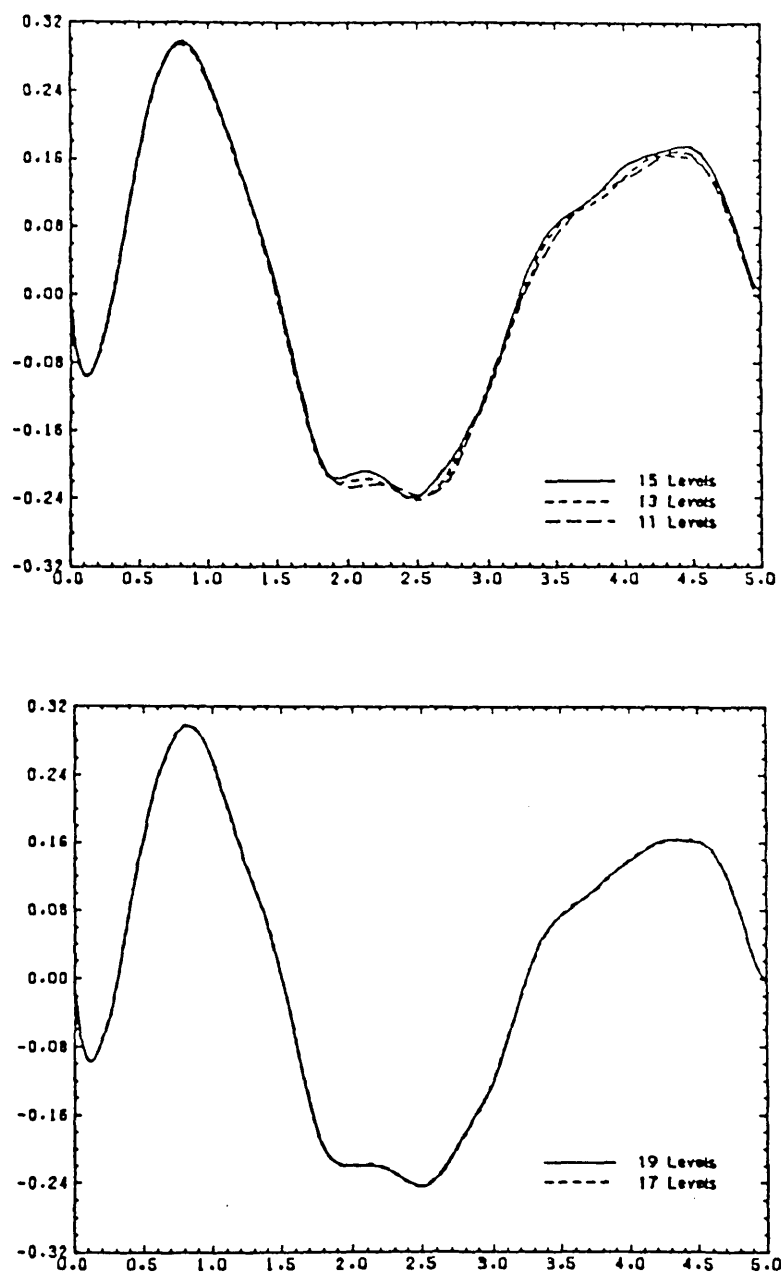


Figure 2.3.5 Structural energy of the canonical FCC band relative to the exact skew rectangular energy for various numbers of levels, of which 10 are exact. (Termination technique).

sections. The structural energy is more highly dominated by the contributions from the neighbour environments closest to the central atom than is the density of states.

The clusters from which the FCC coefficients used here were calculated were constructed from a certain number of hopping shells. Their symmetry, therefore, is that of the point group of the lattice. We have investigated the effects of cluster shape by constructing spherical and cubic clusters. These may be considered as being composed of a cluster of hopping shells with additional atoms attached to the surface; if the embedded hopping shell cluster contains up to shell N , then N pairs of the spherical or cubic coefficients will be exact. We find that using these clusters gives a few coefficients beyond the N th level which have only small deviations from the exact. However, if we were to take the additional atoms and distribute them about the surface of the embedded cluster so as to form complete hopping shells, then we would obtain approximately the same number of additional coefficients - which are now exact.

The foregoing results lead us to propose the following rule of thumb for the use of the termination technique. Because the quantities obtained with this technique are quickly convergent, and since inexact levels have such a great effect, we suggest that computer store and time be minimised by using clusters that contain only a certain number, N , of hopping shells. The recursion should then be allowed to proceed only to the N th step giving the first N pairs of continued fraction coefficients, which are all exact. With the termination technique described here, these coefficients should give good representations of the density of states and structural energies. For larger clusters of about 10 or more shells, then perhaps one or two inexact levels could

be included in the fraction.

§2.4 Conclusions

We have presented and demonstrated here a new technique which determines parameters a_c , b_c to be used in the square root terminator for any number of coefficients describing a connected band. Available to potential Users as FORTRAN routines, it provides an automatic determination of a_c , b_c whose use in the terminator yields reliable and quickly convergent densities of states and structural energies from small, computationally inexpensive clusters. We have presented reasons why this technique should be preferred to the Cambridge method. It should be stressed that the Cambridge method is a general procedure applicable to the coefficients describing any finite band whereas the termination technique as here developed is applicable only to connected bands. Since bands with a single gap often occur in real situations, we will consider in Chapter 3 the extension of this termination technique to sets of coefficients describing such bands.

Chapter 3. The Single Band Gap.

In this Chapter we consider the extension of the previously developed ideas to the situation where the band under consideration contains a gap. We first indicate the effect of the band gap on the behaviour of the continued fraction coefficients and describe the terminator appropriate to this case. The termination technique as extended to the single band gap is then developed using two simple model bands as illustration. Some complications in the application of the technique are then discussed in detail, with particular reference to the practical aspects of its use.

§3.1 Behaviour of the Coefficients in the Presence of a Gap.

Gaspard and Cyrot-Lackmann (1973) found empirically that internal singularities in a band give rise to damped oscillations in the coefficients. They found that the frequency of the oscillation depends on the position of the singularity and the damping is inversely related to its strength. Hodges (1977) (see also Bylander and Rehr (1980)) has proved this relation in a simple perturbation analysis. As a form of particularly strong singularity, a gap in the density of states induces undamped oscillations in the continued fraction coefficients. Gaspard and Cyrot-Lackmann (1973) first found that the coefficients for the sp^3 bands of diamond had two limiting values: the odd coefficients a_{2n+1} , b_{2n+1} tend to a different asymptotic limit from the even coefficients a_{2n} , b_{2n} . Bylander and Rehr (1980) considered the effect of a sinusoidal asymptotic behaviour for the coefficients and were then able to derive an expression for the density of states near the gap. In their investigation of the intermetallic compounds TiFe and CuZn, Glaser and Rennert (1981) found that the coefficients for CuZn exhibit strong asymptotic oscillations which lead to a gap in the density of states.

A comprehensive discussion of the behaviour of the coefficients in the presence of a gap has now been given by Turchi et al. (1982). They find that for the case of a single gap, the a_n , b_n are given by periodic elliptic functions of n which are generally incommensurate with n , and are able to derive an analytic expression for the asymptotic tail of the fraction.

In their §5.2, Turchi et al. (1982) give two equivalent forms for the terminator depending on whether (a_{n-1}, b_n) or (a_n, b_n) are the

last known pair of coefficients. If the last level of the fraction is

$$E - a_{n-1} - t(E) \quad (3.1.1)$$

then

$$\begin{aligned} t(E) &= \frac{E^2 + A_1 E + A_2 + 2b_n^2 - \sqrt{X(E)}}{2(E + A_1 + a_{n-1})} \\ &= \frac{2b_n^2(E + A_1 + a_n)}{E^2 + A_1 E + A_2 + 2b_n^2 + \sqrt{X(E)}} \end{aligned} \quad (3.1.2)$$

for the two cases above. In terms of the parameters a, W, g, G (see Figures 3.1.1 and 3.1.2), the constants A_1, A_2 are:

$$\begin{aligned} A_1 &= -(a + g) \\ A_2 &= \frac{1}{2} (2ag - W^2 - G^2) \end{aligned} \quad (3.1.3)$$

and

$$X(E) = (E - E_1)(E - E_2)(E - E_3)(E - E_4) \quad (3.1.4)$$

where $E_1, \dots, E_4$ are the band and gap edges. The square root gives two branch cuts on the real axis, on which $\text{Im}(t(E)) \neq 0$ leading to two continuous bands for the density of states. In our work we use only the second of (3.1.2) for the terminator since, as will be evident later, the first does not have a useful form.

The termination technique will be considered in detail in the following sections; in the rest of this section we demonstrate why the proper terminator should be used when there is a gap. We investigate the efficacy of the Cambridge method and the terminator method as

developed for the connected band in Chapter 2 when dealing with asymptotically periodic coefficients.

The two model bands used as examples throughout this Chapter are what we will call "split rectangular" bands: they consist of two rectangular sub-bands separated by a gap. We use both the simple symmetric bands, Figure 3.1.1, and the asymmetric bands, Figure 3.1.2. The continued fraction coefficients have been obtained from the moments (which can be calculated exactly) by the procedure (Wall 1948 p196) described in 1.2.4. This procedure is applicable to sets of moments derived from bands with gaps, but its numerical instability increases with the width of the gap. Only about 20-25 pairs of coefficients are obtained for each band. The coefficients are shown in Figures 3.1.3 and 3.1.4, where the oscillatory behaviour may clearly be seen.

The Cambridge method is applicable to all spectra (Nex 1978; Haydock 1980). We have, therefore, used it to calculate the density of states and structural energy for the asymmetric split rectangular band. Figure 3.1.5 shows the results obtained for $n(E)$ and Figure 3.1.6 those for $U(N)$ relative to the exact energy which is given by:

$$U(E) = \begin{cases} \frac{h_L}{2} (E^2 - (a - W)^2) & a-W \leq E < g-G \\ \frac{h_L}{2} ((g - G)^2 - (a - W)^2) & g-G \leq E \leq g+G \\ \frac{h_L}{2} ((g - G)^2 - (a - W)^2) + \frac{h_U}{2} (E^2 - (g + G)^2) & g+G < E \leq a+W \end{cases}$$

$$N(E) = \begin{cases} h_L(E - (a - W)) & a-W \leq E < g-G \\ h_L(g - G - (a - W)) & g-G \leq E \leq g+G \\ h_L(g - G - (a - W)) + h_U(E - (g + G)) & g+G < E \leq a+W \end{cases}$$

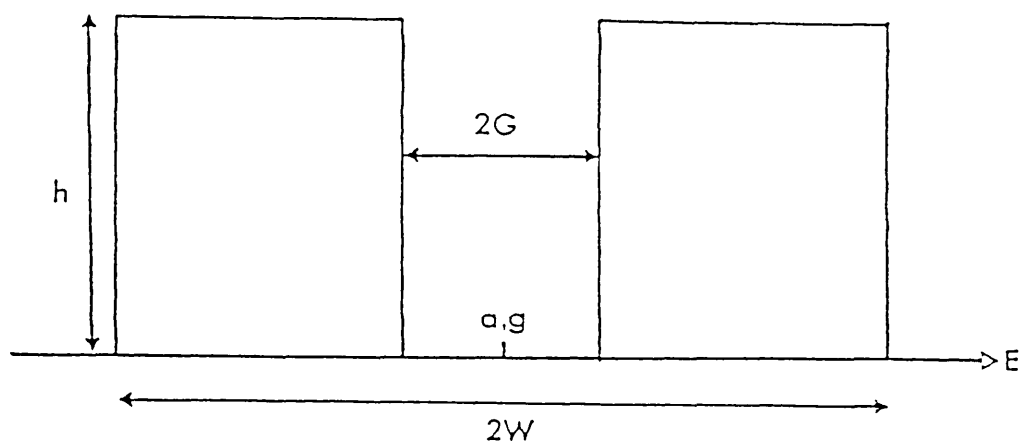


Figure 3.1.1 The symmetric split rectangular band.
 The parameters used are: $a = 0$, $W = 2.0$,
 $g = 0$, $G = 0.5$.

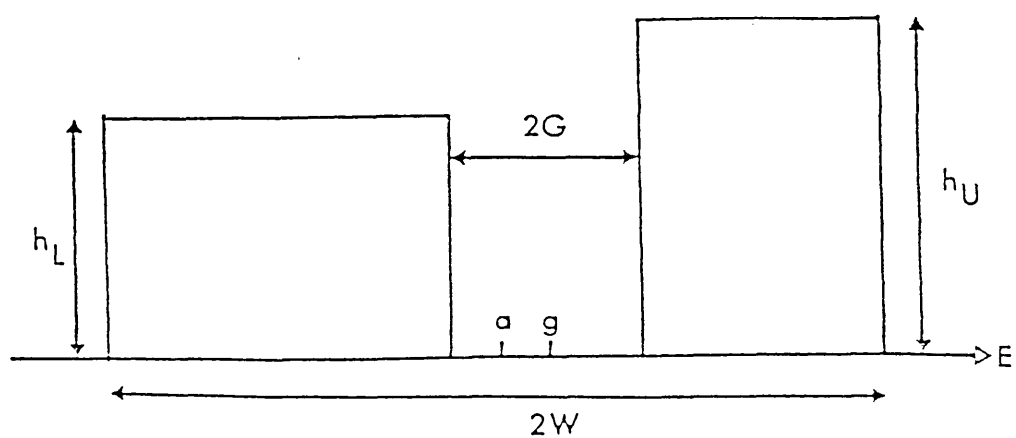


Figure 3.1.2 The asymmetric split rectangular band.
 The parameters used are: $a = 0$, $W = 2.0$,
 $g = 0.2$, $G = 0.5$,
 $h_u/h_L = 1.5$.

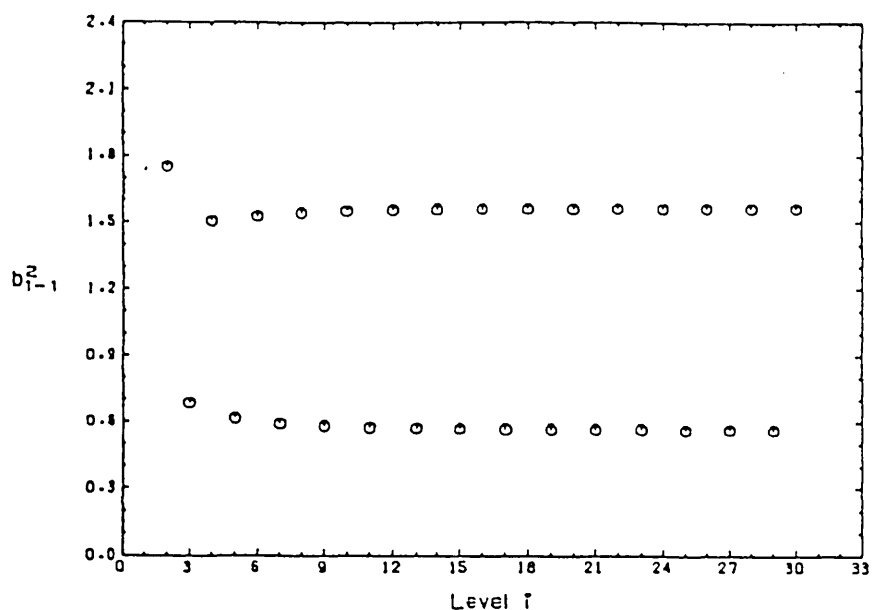


Figure 3.1.3 The coefficients, b_{i-1}^2 , for the symmetric split rectangular band.

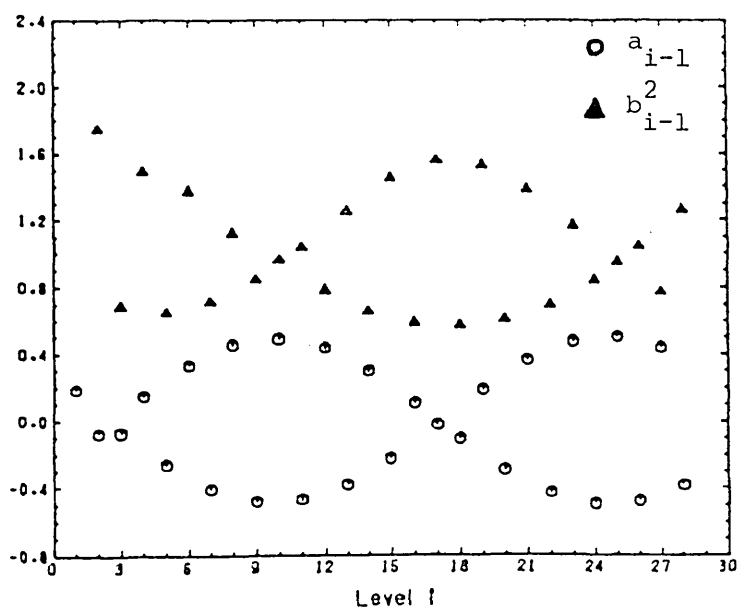


Figure 3.1.4 The coefficients, a_{i-1} , b_{i-1}^2 for the asymmetric split rectangular band.

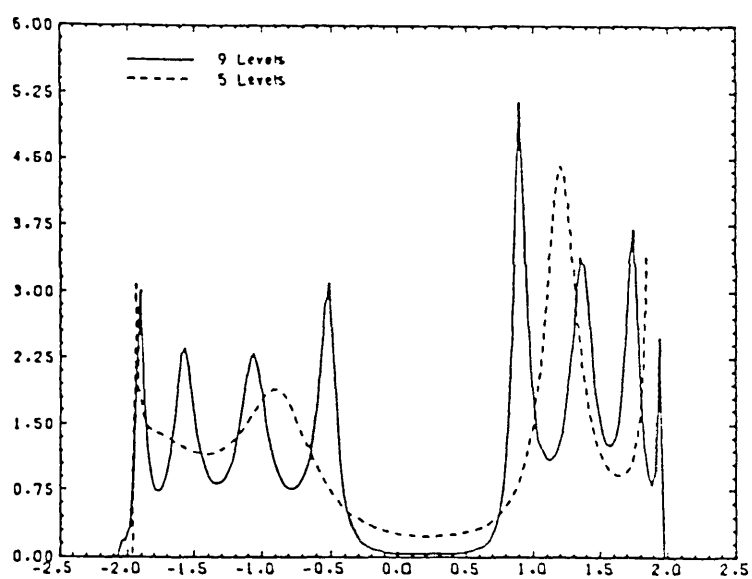


Figure 3.1.5

Convergence of the Cambridge approximation
to the asymmetric split rectangular density
of states.

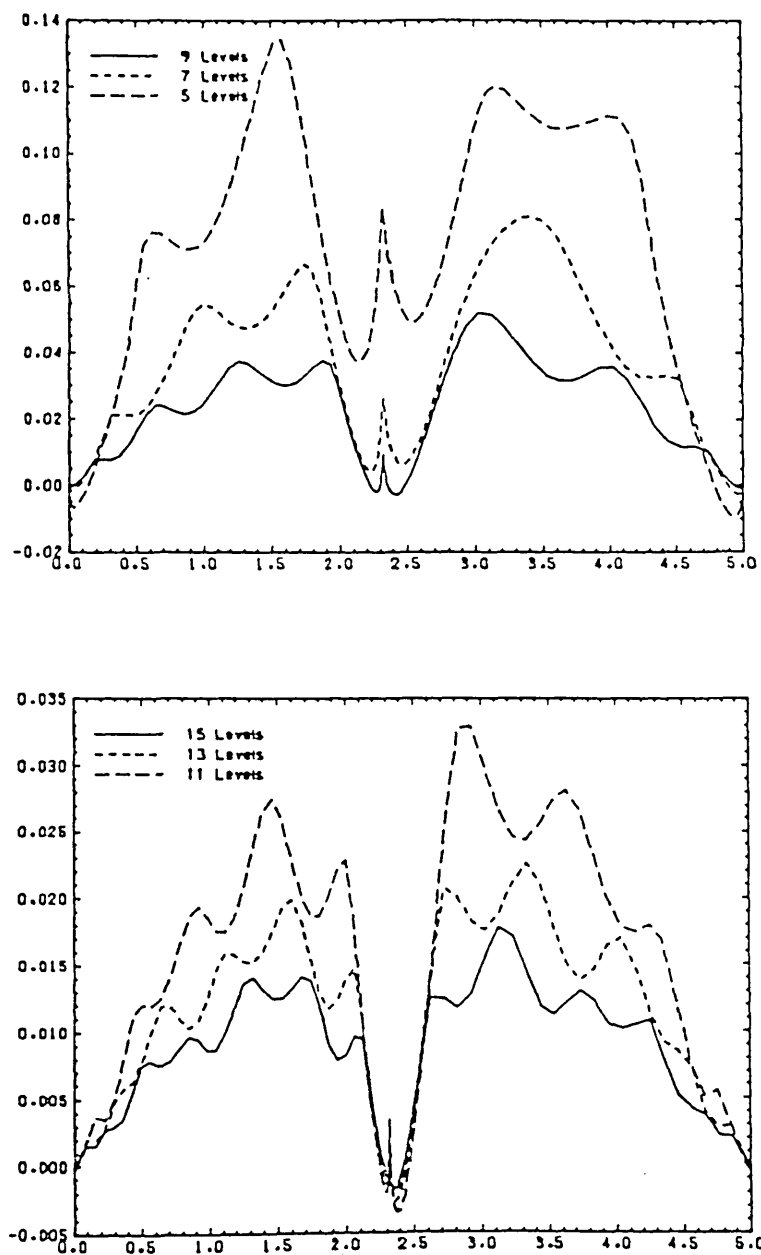


Figure 3.1.6

The structural energy of the symmetric split rectangular band relative to the exact energy. (Cambridge method).

The immediately obvious failing of the Cambridge method is that the $n(E)$ within the gap is non-zero, although the magnitude does tend towards zero as more levels are included in the fraction. The stable form of the density of states with many levels does not have $n(E)$ constant within the sub-bands. Also, the number of zeros of $\Delta U(N)$ indicates that, once again, the moments are not preserved.

We have naively used the termination procedure developed in Chapter 2 on the coefficients for the asymmetric band. The terminating coefficients, a_c , b_c , we then obtain are shown in Figure 3.1.7. The densities of states resulting from termination with these coefficients in the square root terminator (2.2.4) are shown in Figure 3.1.8. These spectra, consisting of roughly as many peaks as the number of levels, are clearly no better a representation of the true density of states than those produced by the Cambridge method. The $\Delta U(N)$ in Figure 3.1.9 indicate, however, that the moments are at least preserved with the terminator. The connected band technique, of course, assumes the wrong asymptotic behaviour of the coefficients, and thus will be unable to reproduce the correct behaviour of the Greens function, particularly near the gap edges.

We continue in the next section to describe the correct terminator for the band with a single gap, and consider the extension of our termination technique to this case.

§3.2 Basics of the Termination Technique Developed on a Simple Example.

In this section we develop the extension of the ideas of the previous Chapter to the situation of a single band gap. Additional

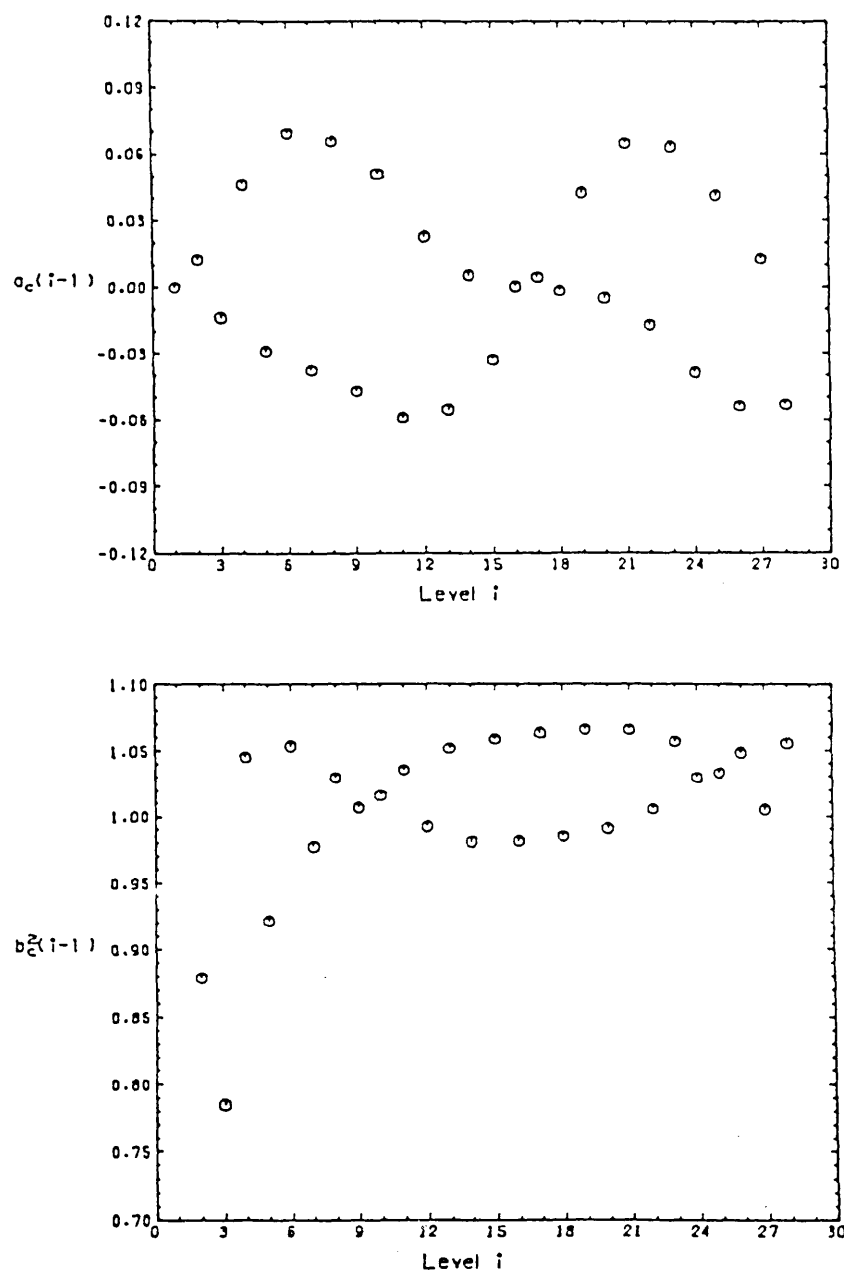


Figure 3.1.7

Connected band terminating parameters a_c , b_c for the asymmetric split rectangular band coefficients.

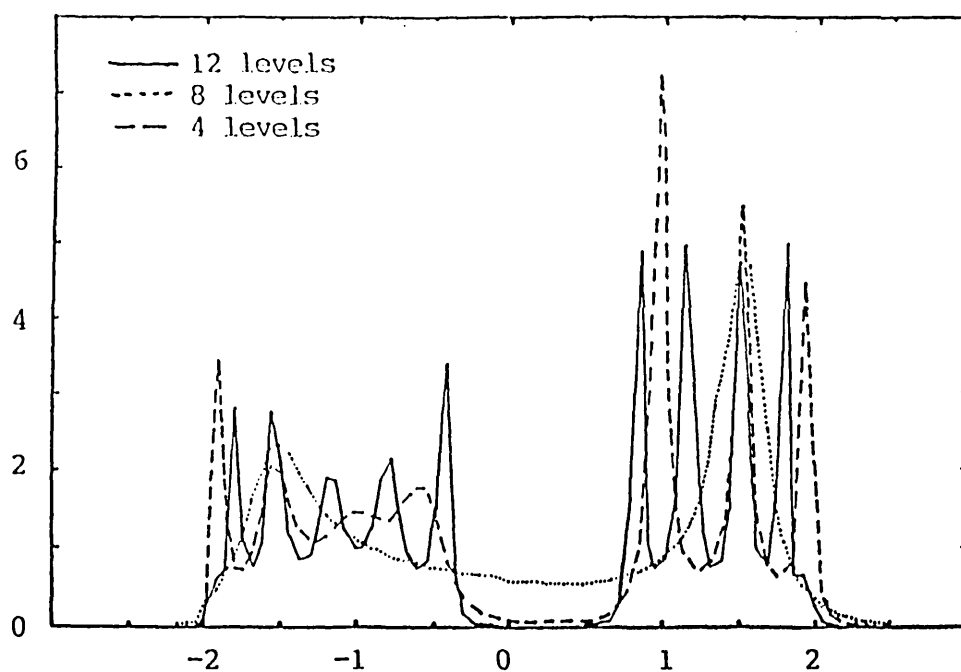


Figure 3.1.8 Densities of States for the Asymmetric Split Rectangular Band with connected band terminators.

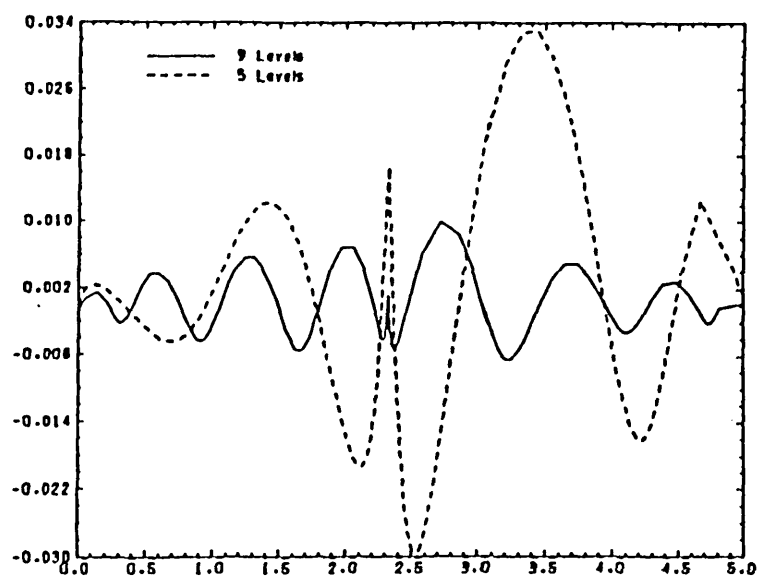


Figure 3.1.9 Structural energy of the asymmetric split rectangular band relative to the exact, calculated with the connected band square root termination technique.

complications arising from this application will be discussed in section 3.3. Here we use the symmetric split rectangular band as an example and restrict our attention to only certain numbers of levels so as to avoid the problems discussed later in §3.3.

3.2.1 The Basic Termination Technique.

We show first that a simple extension of the criterion used in 2.2.2 can be used here to determine the gapwidth and bandwidth. We will use the symmetric split rectangular band for illustration throughout this section because it has $a_i = 0$ for all i , and because the terminators a , g will both vanish due to the symmetry of the band. In this section, therefore, we are concerned only with the (half) gapwidth G and the (half) bandwidth W .

We calculate the weight in the symmetric split rectangular band,

$$\mu_0 = \int_{-\infty}^{\infty} n(E) dE \quad (3.2.1)$$

as a function of both the bandwidth, W , and the gapwidth, G , using the terminator (3.1.2). In Figure 3.2.1 we show the weight as a function of G at $W = 2.0$ and as a function of W for $G = 0.5$. We also show on these graphs the positions of the delta functions obtained by truncating the fraction at 8 levels - their positions are given by $G_i = \pm \epsilon_i$ and $W_i = \pm \epsilon_i$, the positive(negative) sign being used when $\epsilon_i > 0$ ($\epsilon_i < 0$). Because of the symmetry of the band, the line at G_i or W_i in Figure 3.2.1 represents two delta functions, at $\pm \epsilon_i$, and its height is $2w_i$. The form of these curves is the same as for the

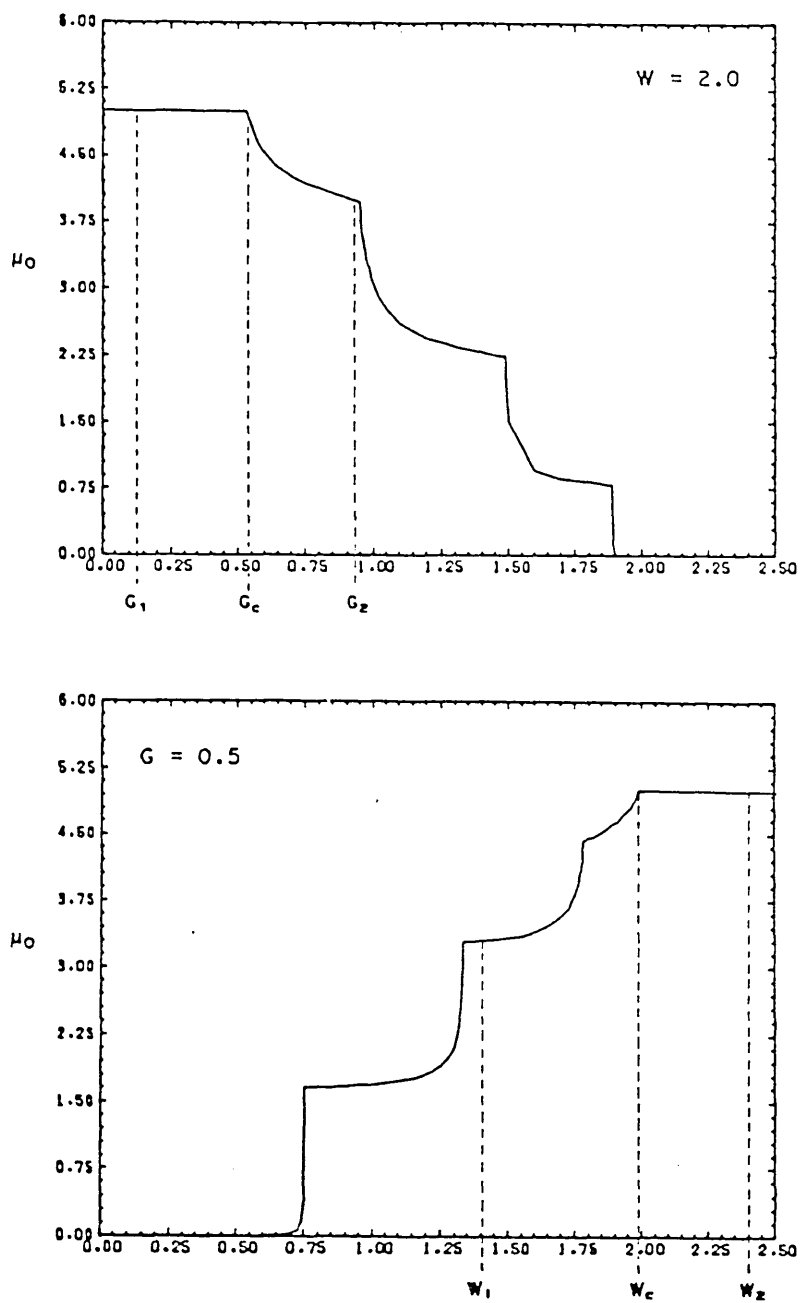


Figure 3.2.1 Weight in the symmetric split rectangular band as a function of G and W . (8 levels).

connected band (Figure 2.2.5) and in Figure 3.2.2 it can be seen that the mechanism of weight loss is also the same as for the connected band. This Figure shows the density of states calculated using the band gap terminator and the values of W and G shown in Figure 3.2.1. Once again, weight is lost into delta functions, either outside the band or within the gap, according to our choice of W and G . At those values of W or G corresponding to the cusps in Figure 3.2.1 the density of states at the gap or band edges diverges. Although in Figure 3.2.1 we have chosen $W = 2.0$ and $G = 0.5$ (which are their true values), the arguments above are true in general, provided that we do not choose G large enough and W small enough that delta functions have been excluded both outside the band and within the gap. We can, in fact, plot in the W - G plane the locus of the cusp at which μ_0 is just equal to 5. In Figure 3.2.3 we have done this for 8 levels of the symmetric split rectangular band. Above and to the left of the line $\mu_0 = 5$, below and to the right $\mu_0 < 5$.

Figures 3.2.1 to 3.2.3 indicate that we should use a simple extension of the criterion of Chapter 2 : we wish to find the minimum bandwidth and the maximum gapwidth consistent with no loss of weight from the band.

As indicated in Figure 3.2.2, at W_c and G_c the density of states at (respectively) the band and gap edges diverges. We now demonstrate that this fact and the extended criterion above allows us to calculate, for any set and any number of coefficients, the values of G_c and W_c .

We first investigate the value of the terminator (3.1.2) at the band and gap edges. Substituting $E = \pm W$ and $E = \pm G$ into (3.1.2) we obtain

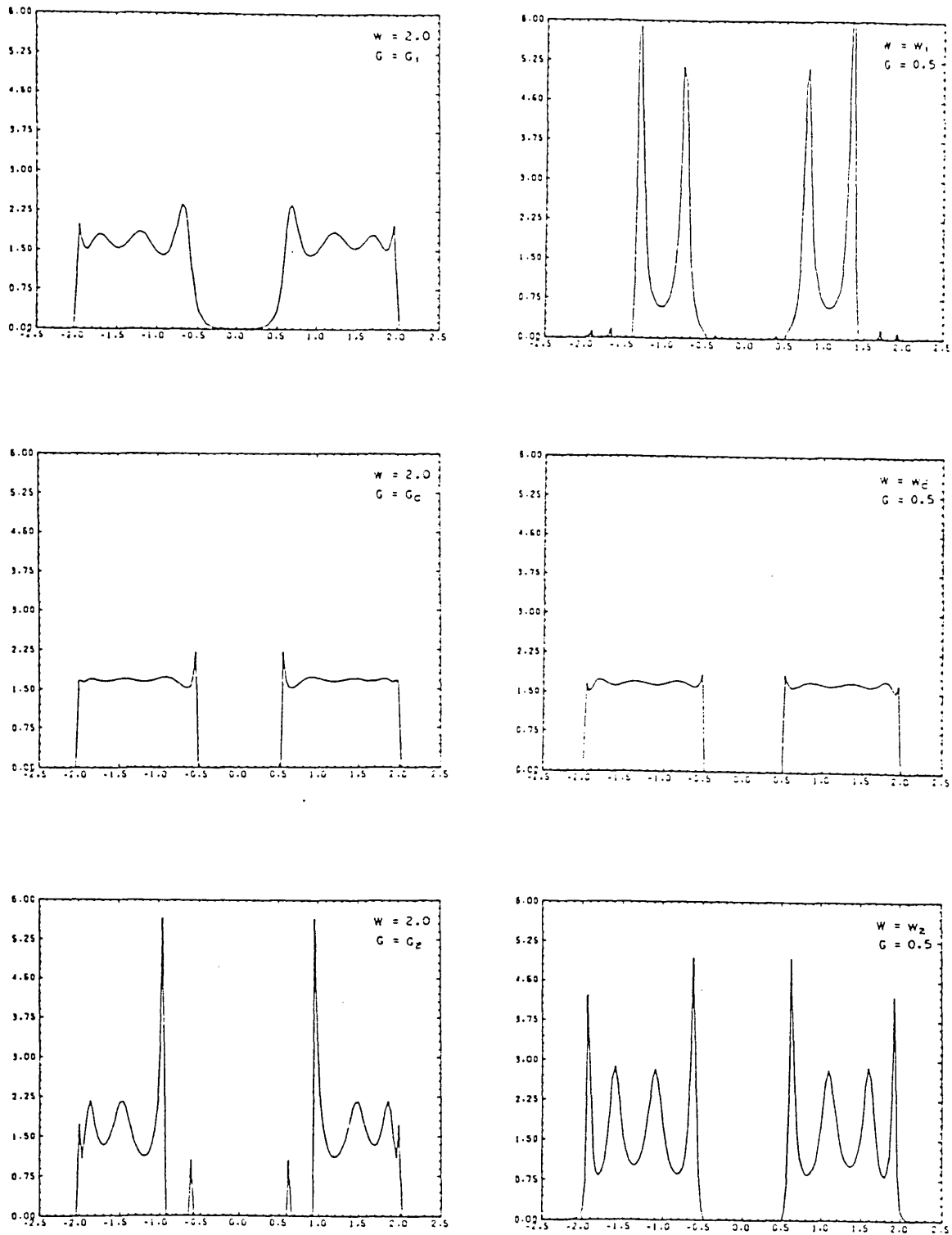


Figure 3.2.2

Density of states for the symmetric split rectangular band with various values of G and W .
 $\text{Im}(E) = 10^{-4}$ outside band. (8 levels).

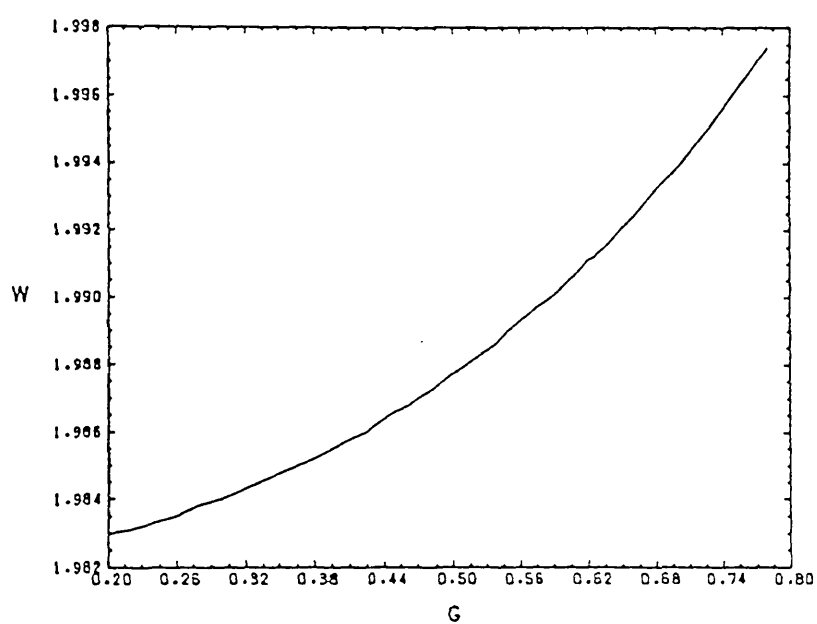


Figure 3.2.3 Locus of the $\mu_0 = 5$ cusp in the W-G plane for the symmetric split rectangular band. (8 levels).

$$t(\pm W) = \frac{4b_{n+1}^2 (a_{n+1} \pm W)}{W^2 - G^2 + 4b_{n+1}^2} \quad (3.2.2)$$

$$t(\pm G) = \frac{4b_{n+1}^2 (a_{n+1} \pm G)}{G^2 - W^2 + 4b_{n+1}^2}$$

The square root vanishes at gap and band edges. These expressions may easily be manipulated into a form in which their use becomes evident:

$$t(\pm W) = \frac{4b_{n+1}^2}{\pm W - a_{n+1} - \frac{G^2 - a_{n+1}^2 - 4b_{n+1}^2}{\pm W + a_{n+1}}} \quad (3.2.3)$$

$$t(\pm G) = \frac{4b_{n+1}^2}{\pm G - a_{n+1} - \frac{W^2 - a_{n+1}^2 - 4b_{n+1}^2}{\pm G + a_{n+1}}}$$

It is at this point that we see why only the second form of (3.1.2) for the terminator has been used: the first cannot be manipulated into this continued fraction form and is, therefore, of no use in the following development. Thus, if we make the substitutions $E = \pm W$, $E = \pm G$ throughout the fraction we find that the Greens function at the gap and band edges is given by a finite continued fraction and can therefore be written:

$$G_{00}(\pm G) = [(\pm G - H_G(W))^{-1}]_{00} \quad (3.2.4)$$

We will only show explicitly the formulae for the gap edges; those for the band edges are easily derived. $H_G(W)$ is the tridiagonal matrix

$$H_G(W) = \begin{pmatrix} a_0 & b_1 & 0 & & & & \\ & b_1 & a_1 & b_2 & & & \\ 0 & b_2 & \ddots & \ddots & & & \\ & & & \ddots & 2b_{n+1} & 0 & \\ & & & & \ddots & & \\ & 0 & & & 2b_{n+1} & a_{n+1} & \beta_{n+1} \\ & & & & 0 & \beta_{n+1} & -a_{n+1} \end{pmatrix} \quad (3.2.5)$$

where

$$\beta_{n+1}^2 = W^2 - a_{n+1}^2 - 4b_{n+1}^2 \quad (3.2.6)$$

We note immediately that for some values of the coefficients and the parameters it is possible for $\beta_{n+1}^2 < 0$. The matrix (3.2.5) is then non-Hermitian and may have conjugate pairs of complex eigenvalues. In all cases investigated, however, this has only occurred for parameters in (3.2.6) and (3.3.4) outside the range of interest. The real part of these complex eigenvalues behaves in a fashion similar to the real eigenvalues and so, in the computer routines, we have treated this real part as a doubly degenerate real eigenvalue when complex eigenvalues occur. It is to be emphasised that this ad hoc safety device has not been needed for any of the sets of coefficients here.

At the eigenvalues of $\pm G - H_G(W)$, the density of states at the gap edges, $G_{00}(\pm G)$, diverges. We call these eigenvalues G_i and note that the G_i for the upper gap edge, $+G$, and the G_i for the lower gap edge, $-G$, are simply related by an inversion through the origin. The G_i are implicit functions of W due to the dependence of the terminator $t(\pm G)$ on W . Similarly, at the eigenvalues of $\pm W - H_G(G)$, where $H_G(G)$ is constructed with $E = \pm W$, $G_{00}(\pm W)$ diverges. These eigenvalues are implicit functions of G , $W_i(G)$, and have the same inversion symmetry

as the G_i . As for the connected band, the W_i of interest are the maximum and minimum (whose magnitudes are equal for the symmetric split rectangular band) since these correspond to the cusp at W_c in Figure 3.2.1 where $\mu_0 = 5$. The eigenvalues G_i of interest are the two, one positive and one negative, with the smallest magnitudes; these correspond to the cusp at G_c in Figure 3.2.1 where $\mu_0 = 5$.

For given W , therefore, we can locate the G corresponding to G_c in Figure 3.2.1 which lies on the $\mu_0 = 5$ curve in Figure 3.2.3. Similarly, for given G we can locate the W lying on the $\mu_0 = 5$ curve. Alternation between the procedures for the gap and band edges, using the output parameters of one as input for the next, gives a means of iteration to self-consistency. From an initial guess (G_0, W_0) the first iteration gives the point (G_1, W_1) which lies on the curve of Figure 3.2.3. Further iterations are performed until the output (G_m, W_m) differs by less than some specified amount from the input, (G_{m-1}, W_{m-1}) . The iteration actually proceeds by the point (G_m, W_m) moving along the curve in Figure 3.2.3 in decreasing steps towards (G_c, W_c) . In all cases examined, this self-consistent iteration converges towards (G_c, W_c) . Note that the curve of Figure 3.2.3 is a section of a surface in the four dimensional space of (a, W, g, G) and the unknown shape of this surface in the two dimensions (a, g) missing from Figure 3.2.3 will also determine the position of the point (G_c, W_c) .

3.2.2 The Terminating Parameters and the Reconstruction of the Density of States of the Symmetric Split Rectangular Band.

Prior to discussing the results obtained with the technique

outlined in 3.2.1 , we give an indication as to how to choose the first estimate of the terminating parameters, (G_0, W_0) , for the self-consistent iteration. If we truncate the fraction at N levels and resolve into partial fractions, (1.2.28), we obtain a representation of the density of states in terms of delta functions, (1.2.29):

$$n(E) = \sum_{i=1}^N w_i \delta(E - \epsilon_i) \quad (3.2.7)$$

where, for the symmetric split rectangular band, the ϵ_i are distributed symmetrically about $E = 0$. We then have an immediate estimate for W as the magnitude of the maximum (or minimum) ϵ_i . In this situation, this is almost trivial, but it is true in general that the extremal ϵ_i give an approximation to the band edges and inspection of the distribution of ϵ_i may also indicate an approximation to the gap edges.

Alternatively, examination of the behaviour of the coefficients may give an indication of the parameters (W_0, G_0) (Turchi et al. 1982), since the bounds on the variation of the coefficients are given by:

$$\begin{aligned} a - G &\leq a_i \leq a + G \\ \frac{W - G}{2} &\leq b_i \leq \frac{W + G}{2} \end{aligned} \quad (3.2.8)$$

where W and G are the true values (W_c , G_c in the asymptotic region). The possible use of these bounds and other methods in Turchi et al. (1982) is limited when only a few levels are used: the coefficients will not begin to obey the laws derived there until they enter the asymptotic region. We, on the other hand, are specifically interested in methods of termination for only a few levels, generally well before the coefficients display fully the asymptotic behaviour.

In Figure 3.2.4 we show the parameters G_c , W_c obtained with our termination technique for the even numbers of levels for the symmetric split rectangular band. We use only the even levels so as to avoid the problems mentioned in the introduction to §3.2. The values of G_∞ , W_∞ are known to be, respectively, 0.5 and 2.0; it can be seen that the values obtained for G_c , W_c do indeed converge steadily with increasing numbers of levels towards the true values. About 5 iterations were required to give an accuracy of 10^{-4} in the self-consistent values, and used about 1.5 CPU seconds (CDC 6000) per level in the calculation. Some optimisation of the routines may be possible.

Using the values of G_c , W_c as given in Figure 3.2.4 in the terminator (3.1.2) leads to the densities of states in Figure 3.2.5. The $n(E)$ obtained should be compared with those obtained with the Cambridge method, shown in Figure 3.1.5. The terminated representation of $n(E)$ is reasonable; for few levels it does truly represent the zero density of states in the gap which the Cambridge method does not. The spurious oscillations in $n(E)$, caused by W_c being smaller than W_∞ and G_c being larger than G_∞ , rapidly lose significance with increasing numbers of levels.

Presentation of the reconstructed $U(N)$ will be left to the following section.

§3.3 The Compleat Termination Technique and a "Real" Application.

In this section we discuss the additional difficulties, mentioned in §3.2, involved in the application of the termination technique to bands with single gaps. We discuss these complexities in detail,

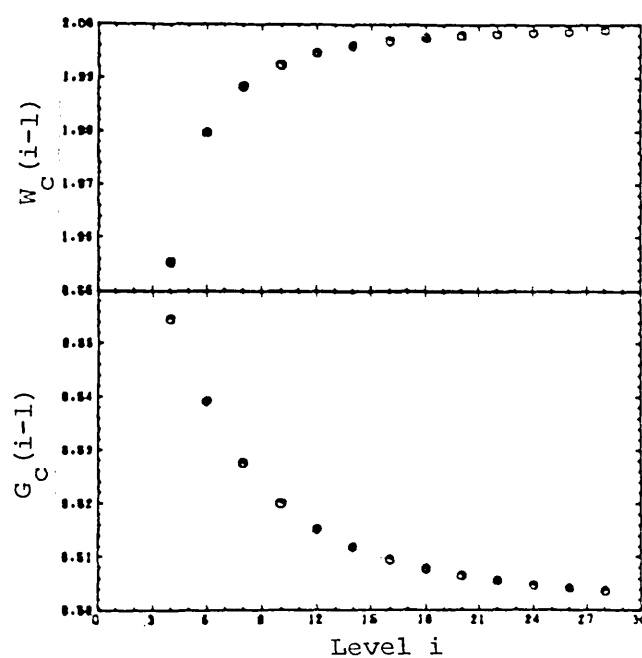


Figure 3.2.4

The terminating parameters G_C , W_C for the even levels of the symmetric split rectangular band.

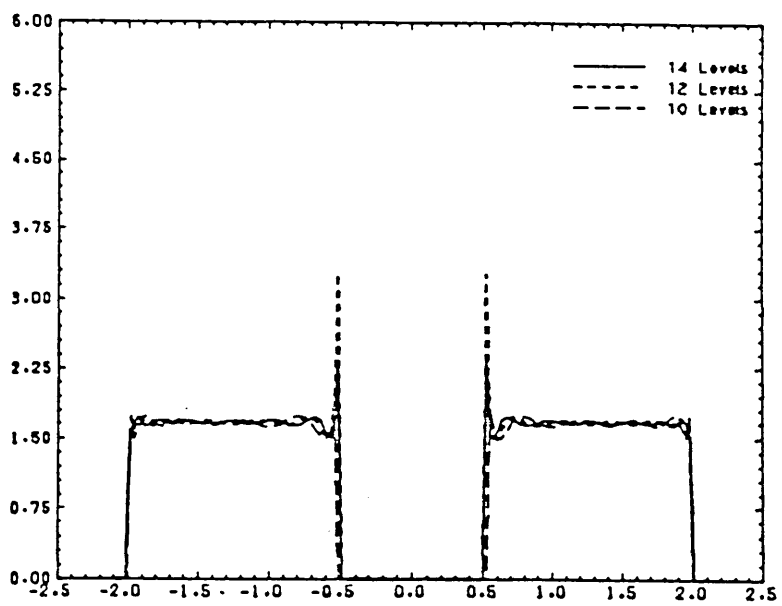
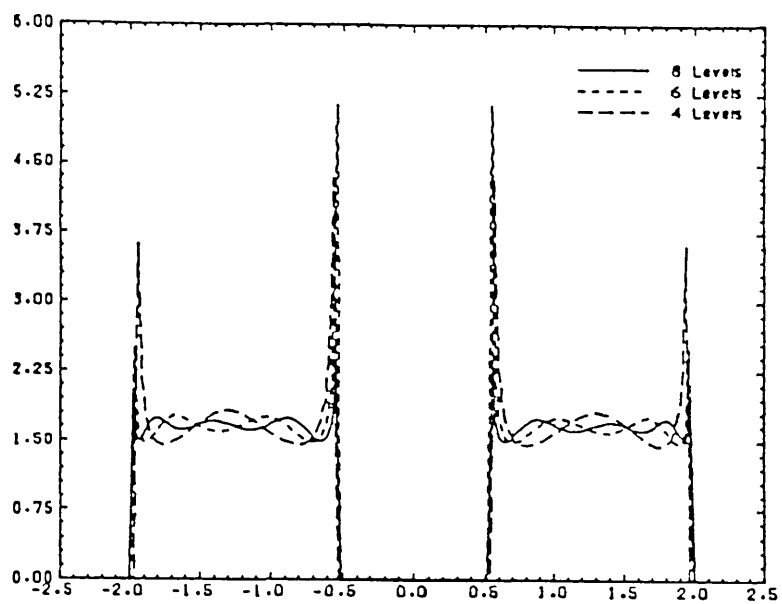


Figure 3.2.5

Convergence of the terminated approximation to the symmetric split rectangular density of states.

explain their implication for the basic termination technique and consider their effects on the resulting parameters and reconstructed quantities. These developments are demonstrated on a model band only slightly less simple than the symmetric band of the preceding sections. Finally, we demonstrate the application of the technique to a set of coefficients describing the "real" band obtained for a model transition metal compound in the CsCl structure.

3.3.1 States in the (True) Gap.

With N levels included in the continued fraction representation of $G_{00}(E)$, the simplest approximation to the density of states is the spectrum of N delta functions at the positions ϵ_i (see equation (1.2.29)). It is possible for one (at most) of these ϵ_i to lie within the true band gap (Turchi et al. 1982). If this is the case for some N , then evidently the arguments of 3.2.1 and 3.2.2 will need to be modified to some degree. This is the reason why only even numbers of levels for the symmetric split rectangular band were considered - there is an ϵ_i in the gap for all odd numbers of levels. The importance of this state on our determination of the terminating parameters lies in how it affects the choice of eigenvalues of $H_G(W)$ to represent the gap edges.

We first point out that the inspection of a spectrum of delta functions, with the intention of estimating the gap position and width, may now be misleading. Ignorance of the true gap edges implies the possibility of an incorrect assessment of the status of the delta symmetric split rectangular band, for all odd numbers of levels there

is an ϵ_i at $E=0$. Since the band gap is relatively wide in relation to the bandwidth, $G/W = 0.25$, this state at the origin is well separated from the sub-bands, whose ϵ_i are relatively closely spaced, and it may reasonably be suspected that this ϵ_i is within the true gap. If, however, the state is close to one of the sub-bands or the gap is relatively narrow then it may not be evident that a particular state is within the gap. This can lead to inclusion of this state into one of the sub-bands and/or improper exclusion of an ϵ_i from one of the sub-bands.

In this section we use as an example the asymmetric split rectangular band shown in Figure 3.1.2, whose coefficients are shown in Figure 3.1.4. For some numbers of levels this band also has states within the true band gap; in fact the behaviour of the ϵ_i as a function of the number of levels in the fraction is shown in Figure 3.3.1. The band is not symmetric and we would thus not expect the terminating parameters a , g to vanish in general. The $G_{00}(E)$ at the gap edges, for example, is then given by

$$G_{00}(g \pm G) = [(\pm G - H_G(g))^{-1}]_{00} \quad (3.3.2)$$

and similarly for $a \pm W$ with the substitutions $G \rightarrow W$, $g \rightarrow a$. The matrix $H_G(x)$ is

$$H_G(x) = \begin{pmatrix} a_0 - x & b_1 & 0 & & & & & \\ & & & 0 & & & & \\ b_1 & a_1 - x & b_2 & & & & & \\ 0 & b_2 & \ddots & \ddots & & & & \\ & & & \ddots & 2b_{n+1} & 0 & & \\ & & & & 2b_{n+1} & \alpha_{n+1} & \beta_{n+1} & \\ & & 0 & & 0 & \beta_{n+1} & \alpha_{n+2} & \end{pmatrix} \quad (3.3.3)$$

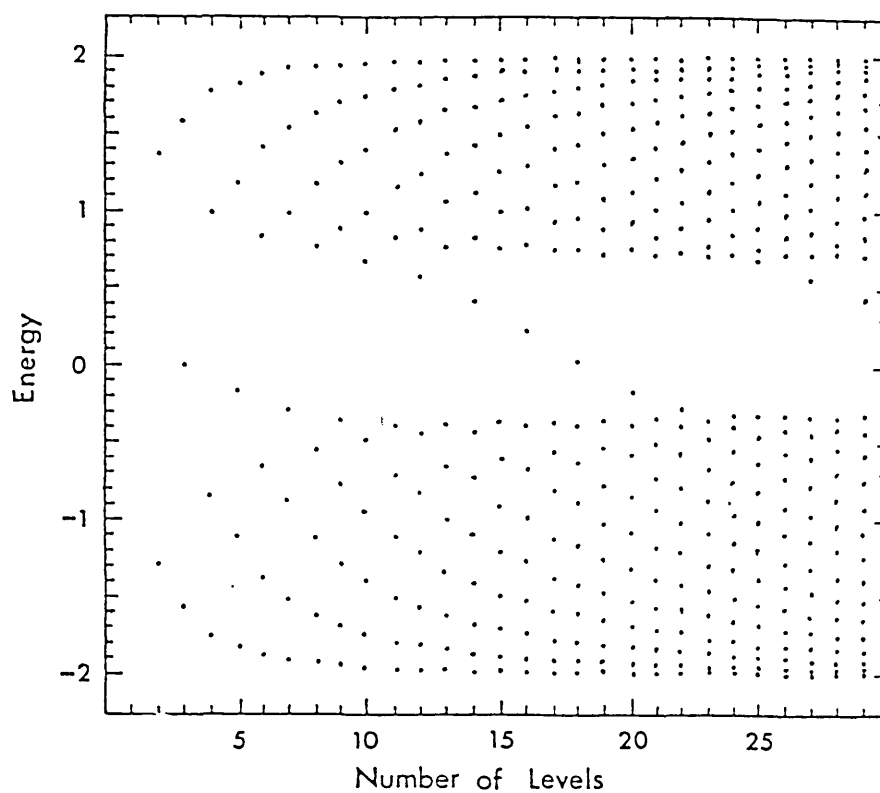


Figure 3.3.1 Truncated fraction delta function positions, ϵ_i , for the asymmetric split rectangular band as a function of the number of levels. The band edges are at $-2.0, -0.3, 0.7, 2.0$.

where, for the gap edges, the additional elements due to the terminator are:

$$\begin{aligned}\alpha_{n+1} &= a_{n+1} - 2g + a \\ \alpha_{n+2} &= a - a_{n+1} \\ \beta_{n+1}^2 &= \alpha_{n+1}\alpha_{n+2} + W^2 - 4b_{n+1}^2\end{aligned}\tag{3.3.4}$$

The elements for the band edges $a \pm W$ are obtained by interchanging g with a and G with W .

Since the band is not symmetric, we must perform the same matching of the magnitudes of the chosen eigenvalues as is performed for the connected band: a_c is determined as that value of a at which

$$W_{\max} = |W_{\min}| = W_c\tag{3.3.5}$$

and, if G_U, G_L represent the eigenvalues of $H_G(W)$ chosen for the gapwidth, then g_c is determined as that value of g for which

$$G_U = |G_L| = G_c\tag{3.3.6}$$

This must be done at each iteration in the self-consistent procedure.

If we regard the state in the gap as being a proper part of the N level representation of the band and thus to be included into our calculations, then we must ensure that our determination of terminating parameters a_c, W_c, g_c, G_c takes this state into consideration. Consider, for definiteness, a spectrum obtained from a truncated fraction which consists of delta functions ϵ_1 to ϵ_n at positive energies and ϵ_{-1} to ϵ_{-m} at negative energies ($n + m = N$). Let us

assume that, were we to know the true gap edges, we would find that ϵ_1 is in fact within the gap. We now construct the terminated tridiagonal matrix for $g \pm G$ corresponding to (3.2.5) and diagonalise to obtain the eigenvalues G_i , $i = 1, \dots, N+2$. These correspond to the gap edge positions, $E_i = g + G_i$, at which the density of states $n(E_i)$ diverges, just before weight is lost from the band into the gap. Notice that the G_i are not symmetric about the origin, so we deal here with those positions of the upper gap edge for which $n(E_i)$ diverges; for the lower gap edge the eigenvalues are $-G_i$, $i = 1, \dots, N+2$ and the positions of the lower gap edge at which $n(E_i)$ diverges are $E_i = g - G_i$. Now, we wish to include this state, ϵ_1 , into our calculations. By reference to Figure 3.3.2 we see that if we choose the lower gap edge to be given by E_L (thus $G_L = g - E_L$) and the upper gap edge to be E_U (thus $G_U = E_U - g$) then the state ϵ_1 is included in the upper band and the total weight in the band is

$$\mu_0 = \sum_{i=1}^m w_{-i} + \sum_{j=1}^n w_j \quad (3.3.7)$$

We then vary g until $G_U = |G_L| = G_c$ at g_c and use these as input to the next iteration. Consistent use of these eigenvalues for the gap edges throughout the iteration to self-consistency leads to final values for the parameters a_c, W_c, g_c, G_c that include the delta function ϵ_1 in the upper sub-band.

If, on the other hand, we regard the state in the gap, although a proper part of the N level truncated approximation to $n(E)$, as inappropriate to the terminator approach to the estimation of the band parameters a, W, g, G , then we should exclude ϵ_1 from consideration.

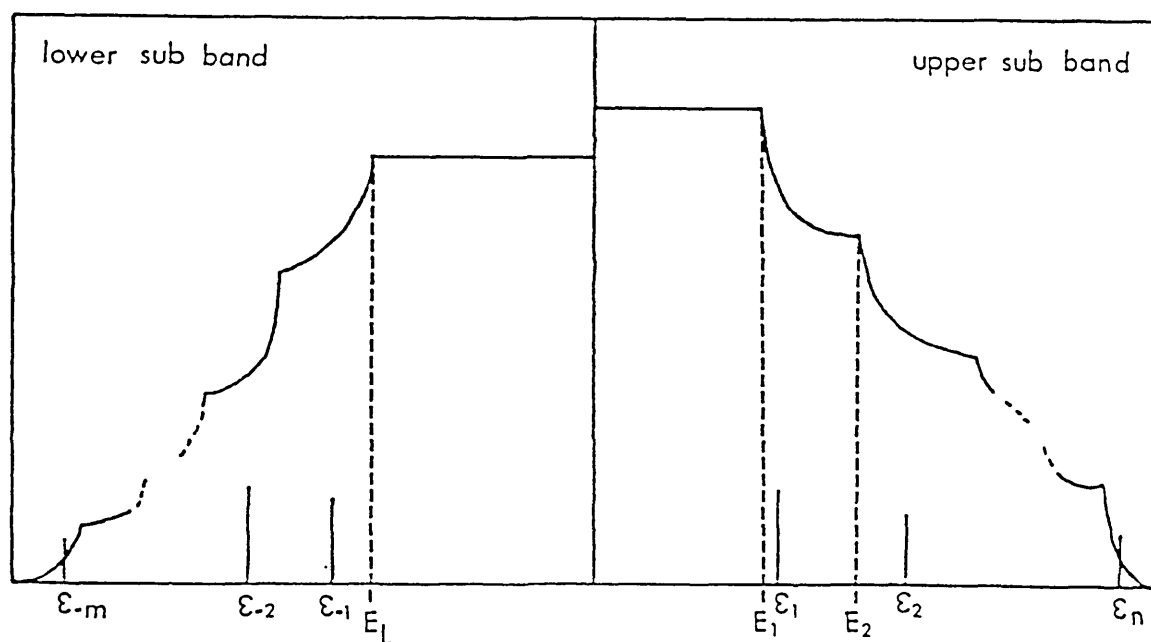


Figure 3.3.2

Schematic diagram of the weight in the upper and lower sub-bands of a band with a gap as a function of G for given a , g , W .

We do this by choosing the upper gap edge as E_2 rather than E_1 . Thus $G_U = E_2 - g$, and the state ε_1 is acknowledged by the method to be within the gap - which is now fitted between the states ε_{-1} and ε_2 , giving in most cases much better values for g_c and G_c . The total weight in the band is now

$$\sum_{i=1}^m w_{-i} + \sum_{j=2}^n w_j < \mu_0 \quad (3.3.8)$$

Moreover, since this gap affects the distribution of weight in the representation of $n(E)$, all the moments of $n(E)$ will not be preserved.

As the number of levels in the fraction increases, the weight of any states in the gap decreases. By level 16 of the asymmetric split rectangular band, the weight excluded in the gap state is so small as to have an effect of less than 0.01% in the first 3 moments.

We are faced, therefore, with a difficult situation. If in all cases we insist on including in the sub-bands the weight of all the ε_i then, when there is an state in the gap, the procedure may return values for g_c and G_c which are substantially awry. How, for example, do we include the weight of the state at $E = 0$ in the gap of the symmetric split rectangular band except by having $G = 0$ for all odd numbers of levels? But if, on the other hand, we exclude the gap state from consideration, then we recover better values for g_c and G_c but, unless we use many levels of the fraction, the moments are not preserved. In this case we would be restricted to using only those numbers of levels for which there is not a state in the gap.

In Figure 3.3.3 we show the excellent convergence of the a_c , W_c , g_c , G_c for the asymmetric split rectangular band found by excluding the gap states from the bands. The asymptotic values are indicated by an

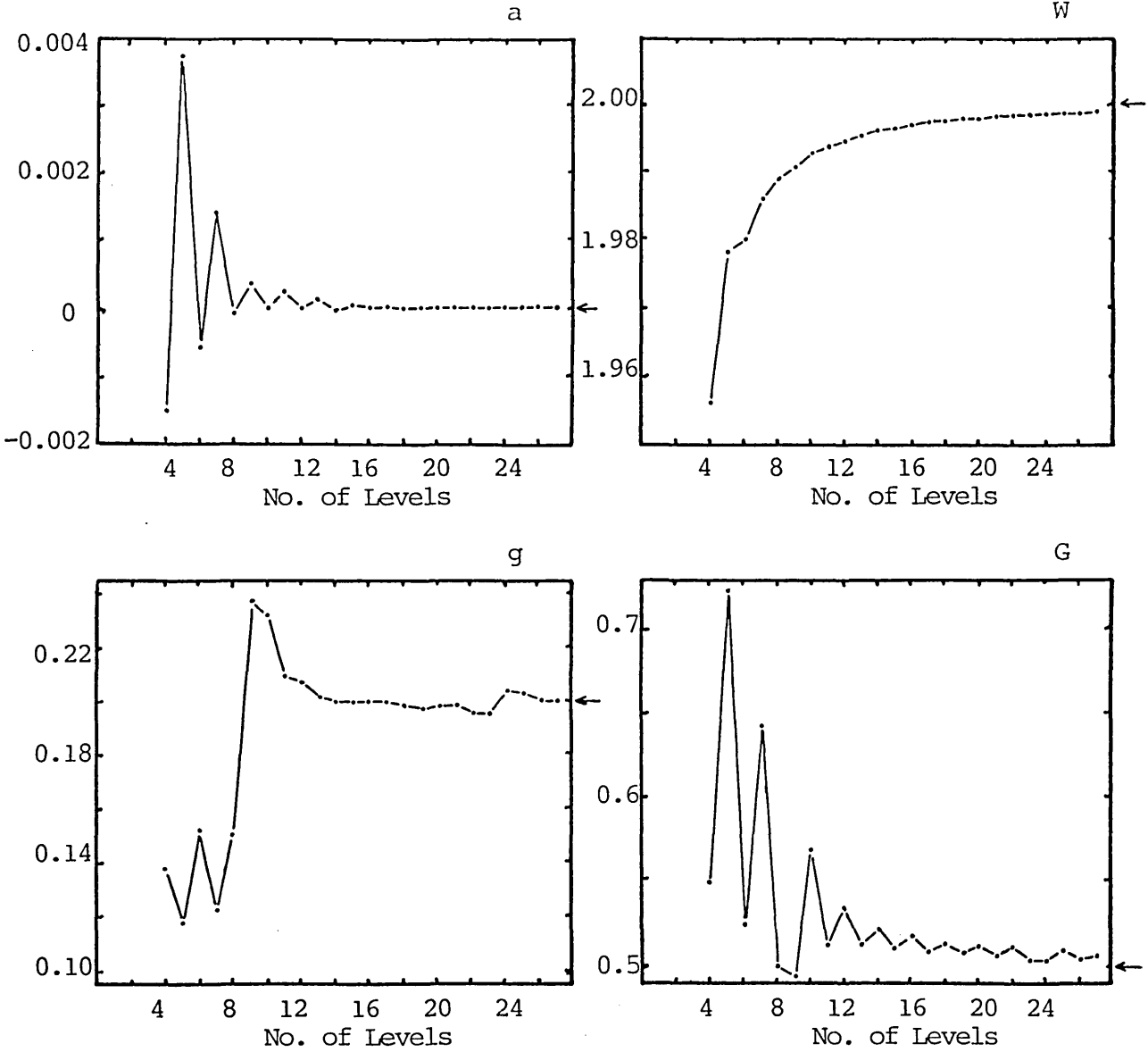


Figure 3.3.3 "Band Gap" Terminators for the Asymmetric Split Rectangular Band.

arrow. The computer routines used to produce these parameters are listed in the Appendix, and some practical details of their use are discussed in section 3.3.2, including some results obtained with the gap state included in one of the sub-bands.

3.3.2 Practical Details

The computer routines implementing the procedure described in section 3.2 and the earlier parts of section 3.3 are listed in the Appendix together with documentation explaining necessary computational details. In this section we cover, in broader terms, the way in which they are to be used, and give some detailed examples.

In section 3.3.1 the situation arising from a state occurring in the true band gap was discussed at length. For our example of the asymmetric split rectangular band the true band edges are known. We were able, therefore, always to choose the position of the gap correctly according to the existence or otherwise of a state in the true gap. As indicated in section 3.3.1, an estimate of the gap position may be gained from inspection of the spectrum of delta functions (1.2.29).

Referring again to Figure 3.3.1 as an example, we see that for a given number of levels there may be a state lying almost centrally in a gap with only a small weight, w_1 . This would probably indicate treating it as a state within the true gap and

thus entering a gap into the routines that excludes this state. Equally, though, for some numbers of levels we may find no clear evidence of one state being within the gap, as for example for 12 levels of Figure 3.3.1. If in this situation we were to choose, wrongly, that there is not a state in the gap, what results would this give in the computer routines, and would it be clear that an incorrect choice had been made? Or, possibly, we might choose a state to be within the gap when, in fact, for that number of levels there is no state within the gap; will there also be some indication that this incorrect choice had been made?

In order to illustrate how the method copes with these incorrect choices, we have compiled in Table 3.3.1 a list of deliberate incorrect choices made for various numbers of levels for the asymmetric split rectangular band, and the results obtained from the computer routines in the Appendix.

For 16 levels, when a state is almost centrally placed in the gap, the routines find self-consistent values for the parameters. On inspection, however, we find the the position of the gap has shifted from the input. When the gap state is included into the upper sub-band, the gap "jumps" over a delta function into the lower sub-band. Similarly, when included into the lower sub-band, the gap shifts into the upper. In both cases, the self-consistent gap appears between delta functions different to those initially guessed. A similar effect is seen at 14 levels. When the state is close to the gap edge, as for 10 and 7 levels, we recover from the routines sensible values for g_c and G_c , although the gapwidth is

No. of levels	Comments	Self-consistent parameters				μ_0
		a	W	g	G	
7	Inclusion of ϵ in gap at -0.28 into lower band	.001	1.985	.353	.390	5.00
9	Exclusion of ϵ at -0.35 from lower band	.000	1.991	.102	.631	4.79
10	Inclusion of ϵ in gap at 0.68 into upper band	.001	1.993	.108	.437	5.00
13	Exclusion of ϵ at -0.38 from lower band	-.001	1.996	.094	.612	4.81
14	Inclusion of ϵ in gap at 0.43 into upper band	.008	1.999	-.465	.028	4.48
16	Inclusion of ϵ in gap at 0.23 into upper band	.008	1.997	-.543	.155	5.00
16	Inclusion of ϵ in gap at 0.23 in to lower band	-.007	1.993	.912	.133	5.00

Table 3.3.1 Effect of incorrect choices for the gap position on the results obtained with the computer routines.

perhaps a little small compared with the available region between the delta functions.

If, alternatively, a delta function within one of the sub-bands is treated as being in the gap, as for 13 and 9 levels, the routines find self-consistent values that seem reasonable. In this case the clue as to the incorrect choice of gap position must be the weight, μ_0 , which will be found to be less than the correct weight.

These results indicate that should an incorrect choice of gap position be made, the results obtained from the computer routines should be such as to inspire enough doubt in the User's mind that an alternative choice may be tried. Even in the most extreme cases, it is believed that comparison of the results obtained for a few possible choices of gap position, if necessary for two adjacent numbers of levels, will indicate quite clearly the correct choice.

It is unfortunate that the routines for the determination of the terminating parameters for the band with a single gap are not automatic in the same sense as those for the connected band. This is clearly a consequence of the additional complexity introduced in the form of states in the gap and (possibly) non-Hermitian matrices. Rather than attempt to devise some algorithm to make the routines fully automatic, it was felt that the User would be the best judge of the reasonableness of the results obtained. It is possible that greater understanding of the occurrence and role of the state in the gap may lead to advances in automation of the computer routines.

Chapter 4. Electronic Structure and Structural Stability

In this Chapter we consider the role of the electronic structure in the structural stability of the pure transition metals and of transition metal compounds. We show that for the transition metals the dominant contribution is the d band structural energy, which is calculable with the recursion method and our termination technique.

This then allows us to discuss calculations of the structural energy for the canonical d bands for the BCC, FCC and HCP structures. The calculated structural trend for the transition metals is compared with experiment and previous calculations. The nature of the recursion method, moreover, gives an indication as to which local environment is dominant in determining the structure of the pure transition metals.

These calculations are then extended to consider the transition metal - transition metal AB compounds. The structural energies for the six most common AB compound structures are compared and a theoretical structure map constructed.

4.1 Transition Metal Bonding.

The transition metals are characterised by a fairly narrow d band overlapped by a broad sp conduction band, schematically illustrated with no hybridisation in Figure 4.1.1. Due to the relatively narrow width of the d band and the fact that it must accomodate 10 electrons, the average density of states is substantially higher in the d band than the sp band. There will be some hybridisation between the bands which will tend to push both sp and d states away from the centre of the d band (Gelatt et al. 1977).

Friedel (1969) argued that a good first approximation to the behaviour of the transition metals may be obtained by neglecting the sp band and hybridisation and dealing only with the d band. The cohesive energy of a d band, $n_d(E)$, centred at ϵ_d is given by

$$U_{\text{bond}} = \int_{-\infty}^{E_F} (E - \epsilon_d) n(E) dE \quad (4.1.1)$$

which, with the Friedel approximation of a rectangular d band density of states (see Figure 4.1.2), gives the parabolic behaviour

$$U_{\text{bond}} = - \frac{W}{20} N(10 - N) \quad (4.1.2)$$

observed experimentally for the non-magnetic transtion metals series. Within this simple approximation for the d density of states, Pettifor (1978,1979) was able to develop an analytic theory of the heats of formation of transition metal alloys which gave good

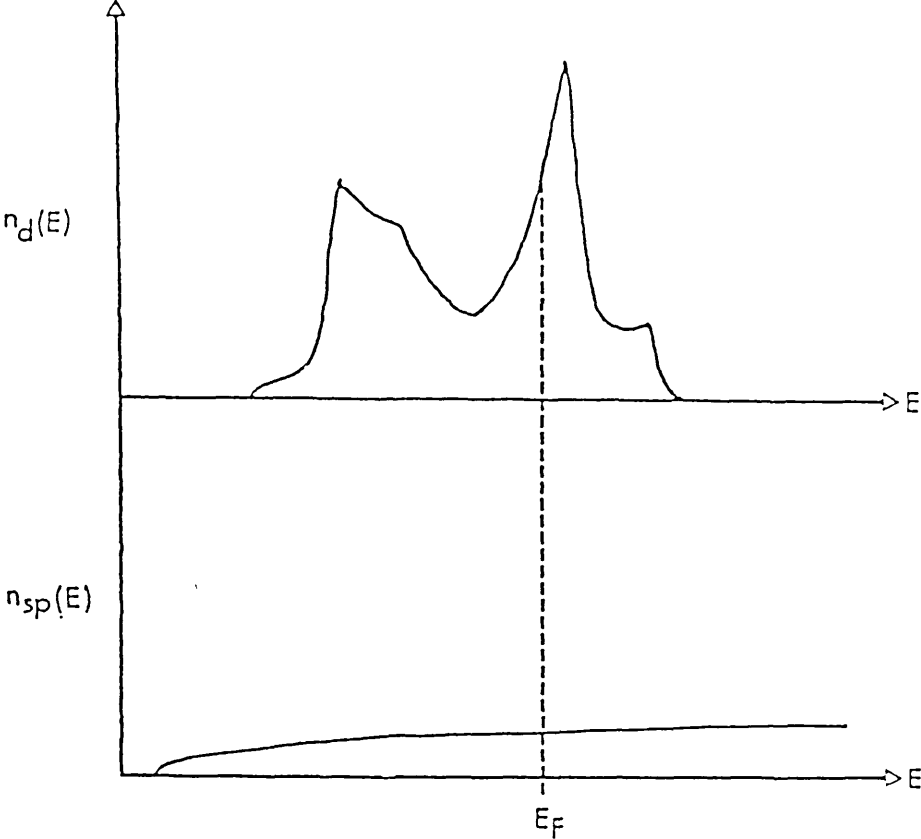


Figure 4.1.1 Schematic diagram of the transition metal band structure.

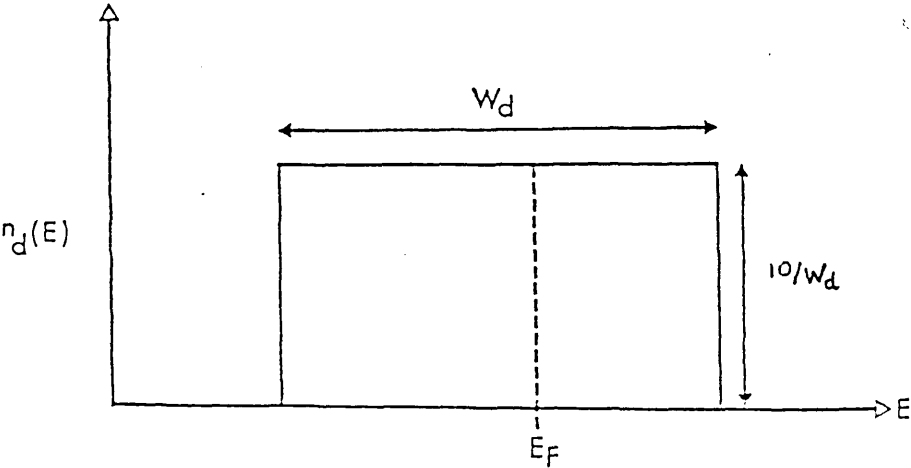


Figure 4.1.2 Schematic diagram of the rectangular band approximation to the transition metal band structure.

agreement with more sophisticated models and provided a microscopic interpretation of Miedema's semi-empirical approach (Miedema 1980; Boom et al. 1976).

Futher calculations using more elaborate models of the d band have confirmed that it provides, for example, the dominant contribution to the cohesive energies of the transition metals (Gelatt et al. 1977), is primarily responsible for the crystal structures of the transition metal series (Pettifor 1970,1977; Ducastelle and Cyrot-Lackmann 1971), the rare-earth series (Duthie and Pettifor 1977) and the Laves phases (Johannes et al. 1978) and gives a good account of the binding energies of transition metal atoms adsorbed onto transition metal surfaces (Cyrot-Lackmann and Ducastelle 1971; Dhanak 1981).

In order to emphasise this importance of the band contribution to the energy, we write the total energy per atom as

$$U = U_{\text{rep}} + U_{\text{band}} \quad (4.1.3)$$

where

$$U_{\text{band}} = \int_{-\infty}^{E_F} E n(E) dE \quad (4.1.4)$$

U_{rep} includes the electrostatic ion-ion Coulomb repulsion and the usual double counting Coulomb and exchange terms (Hohenberg and Kohn 1964; Kohn and Sham 1965).

The band energy can be written in terms of the bond energy as

$$U_{\text{band}} = N_d \epsilon_d + U_d^{\text{bond}} \quad (4.1.5)$$

for an elemental transition metal with atomic energy ϵ_d .

We now apply equation (4.1.3) to the case of the elemental transition metals and the transition metal compounds respectively.

§4.2 The Transition Metal Structures BCC, FCC and HCP.

4.2.1 The Canonical BCC, FCC and HCP Bands.

The bands used for the calculation of the energy differences between the transition metal structures BCC, FCC and HCP are described here.

The continued fraction coefficients are calculated by the recursion method directly from clusters with the appropriate structure. As described in section 1.2.4, for all three structures the hopping parameters used were the "canonical" parameters (Pettifor 1977; Andersen 1975):

$$\text{dd} \begin{Bmatrix} \sigma \\ \pi \\ \delta \end{Bmatrix} = \begin{Bmatrix} -60 \\ 40 \\ -10 \end{Bmatrix} \frac{W_d}{25} (S/R)^5 \quad (4.2.1)$$

with $W_d = 25$. The ratio of the Wigner-Seitz radius, S , to the nearest neighbour distance, R , is dependent only on the structure. For BCC, we allow hopping to both first and second nearest

neighbours, of which there are, respectively, 8 and 6. We therefore have two ratios (S/R_1) and (S/R_2) in BCC. The values of the ratios for the three structures are:

$$\text{BCC: } \begin{cases} S/R_1 = 2/\sqrt{3}(3/8\pi)^{1/3} = 0.568543 \\ S/R_2 = (3/8\pi)^{1/3} = 0.492373 \end{cases} \quad (4.2.2)$$

$$\text{FCC: } S/R = \sqrt{2}(3/8\pi)^{1/3} = 0.552669$$

$$\text{HCP: } S/R = (\gamma\sqrt{3}/16\pi)^{1/3} = \sqrt{2}(3/8\pi)^{1/3} = (S/R)_{\text{FCC}}$$

where we have taken the axial ratio $\gamma = c/a$ for HCP to be the ideal value $\gamma = (8/3)^{1/2}$. With these parameters, the density of states and the structural energy are dependent only on the crystal structure.

The clusters used in the recursion method calculations were of sufficient size that for BCC, FCC and HCP respectively, 19, 20 and 18 pairs of coefficients are exact. The coefficients for the three structures are listed in Table 4.2.1. The "average" coefficients are obtained by initialising the recursion algorithm with an orbital such that the resulting coefficients describe the total density of states on the central atom. For BCC and FCC this orbital is

$$|\phi_0\rangle = \frac{1}{\sqrt{5}} (\sqrt{3}|t_{2g}\rangle + \sqrt{2}|E_g\rangle) \quad (4.2.3)$$

while for HCP it is

$$|\phi_0\rangle = \frac{1}{\sqrt{5}} (\sqrt{2}|A_1\rangle + \sqrt{2}|A_2\rangle + |E_1\rangle) \quad (4.2.4)$$

BCC					
T _{2g}		E _g		Average	
a _i	b _i ²	a _i	b _i ²	a _i	b _i ²
0.0000	3.0000	0.0000	2.0000	0.0000	5.0000
0.1325	50.6959	-4.8221	40.3490	-0.1553	44.6652
1.0125	25.0699	-4.9057	23.4243	-0.0470	28.4995
-0.9263	41.0832	-3.4153	52.5422	-0.3464	61.7148
-0.3337	31.0960	-2.9639	46.3888	-0.3635	45.3443
-1.1271	41.6202	-2.4816	54.1701	-0.2316	49.7217
-0.9510	38.0549	-3.3414	47.7085	-0.2667	46.6989
-2.6682	42.5480	-2.9368	52.3346	-0.3003	52.3417
-3.2229	53.6914	-2.7609	49.1643	-0.2939	45.8354
-3.2848	57.0268	-2.6428	53.8768	-0.2727	51.3014
-1.8351	57.8873	-3.1625	49.9034	-0.2744	47.2773
-3.0433	48.0841	-2.8521	50.6704	-0.2754	50.4541
-3.0254	53.5874	-2.8528	50.8438	-0.3075	47.8097
-3.0401	54.7710	-2.6732	52.6246	-0.2597	50.6439
-2.3065	49.4634	-3.1460	49.7337	-0.2722	47.1646
-2.8801	49.4097	-2.8454	51.0082	-0.2912	50.9065
-2.5551	52.5573	-2.6747	51.6580	-0.2882	48.3337
-3.0298	54.2927	-2.8953	51.7397	-0.2600	49.1373
-2.3867	49.7745	-3.0596	50.1324	-0.2858	49.0382
-2.7982	49.7354	-2.7091	51.1760	-0.2861	49.8957

FCC					
T _{2g}		E _g		Average	
a _i	b _i ²	a _i	b _i ²	a _i	b _i ²
0.0000	3.0000	0.0000	2.0000	0.0000	5.0000
-1.6765	47.0573	-1.4766	41.0754	-1.6030	44.6645
-2.5509	33.2419	-2.2405	35.7504	-2.4270	34.3662
-3.9158	47.1157	-1.8859	42.0764	-3.2245	45.0512
-2.6019	39.5321	-1.9463	41.9711	-2.4686	42.1280
-3.1863	40.0017	-1.9177	40.2071	-2.7015	41.7554
-2.6474	45.2279	-1.6126	42.8404	-2.3307	47.8236
-3.0900	42.9387	-2.2656	43.5084	-2.5690	46.9513
-2.6388	41.3242	-1.6967	40.6440	-2.1969	44.6188
-2.9050	45.1693	-2.4730	44.0729	-2.5984	48.1247
-2.5184	43.5618	-1.9519	43.2999	-2.2759	44.5187
-2.5924	44.8530	-2.3318	45.3679	-2.4984	46.1462
-2.2376	46.1396	-2.6039	45.4130	-2.4768	45.5839
-2.7060	46.3456	-2.2747	45.2097	-2.6458	44.7927
-2.3905	44.2031	-2.5411	45.7597	-2.3400	45.9528
-2.7408	45.5797	-2.2342	45.2339	-2.4593	46.0556
-2.4586	44.4975	-2.3130	44.9468	-2.3329	46.5817
-2.6642	45.1329	-2.3120	44.7900	-2.4667	45.6806
-2.3591	45.2283	-2.3610	45.3357	-2.4195	45.9449
-2.4944	46.2154	-2.5074	44.7449	-2.5949	45.1845

HCP							
A ₁		A ₂		E		Average	
a _i	b _i ²	a _i	b _i ²	a _i	b _i ²	a _i	b _i ²
0.0000	2.0000	0.0000	2.0000	0.0000	1.0000	0.0000	5.0000
-1.6171	45.0733	-1.5431	43.0727	-1.6811	47.0413	-1.6030	44.6644
-3.0960	35.9991	-1.8039	34.8454	-2.4622	29.1161	-2.4686	34.1593
-2.5862	42.9342	-0.9278	31.4587	-3.0655	44.7907	-2.3696	39.1816
-3.0471	39.0981	-1.5212	35.5647	-3.6095	38.6279	-3.0799	40.9513
-2.8239	43.6266	-1.5129	37.0664	-2.1004	40.6457	-2.6804	44.4642
-2.4713	40.4738	-1.7433	37.1028	-3.6309	39.8018	-2.5724	42.5314
-3.0611	41.4689	-1.9592	39.8290	-2.7503	41.1054	-2.4990	42.4456
-2.3072	43.6592	-2.1523	40.9594	-2.7062	39.5945	-2.2237	43.5747
-2.9321	40.4387	-2.4865	41.0542	-3.4241	40.1674	-2.7825	42.6670
-2.3909	43.8257	-2.1398	44.8225	-2.4957	40.7505	-2.1887	45.1786
-2.8254	42.7099	-2.6400	40.3046	-3.1611	41.8239	-2.7633	43.2645
-2.5546	40.7538	-2.0677	42.3546	-2.7136	38.4236	-2.3406	41.8482
-2.6256	44.4858	-2.5588	42.2900	-3.0095	43.4683	-2.6021	44.8411
-2.6739	41.0534	-2.3833	41.8347	-3.6377	39.2454	-2.4973	41.6367
-2.5846	43.1113	-2.5041	44.6907	-3.6265	43.5872	-2.4841	44.3584
-2.6508	42.7643	-2.3271	42.0398	-2.7548	42.1959	-2.5845	43.0731
-2.4347	42.4469	-2.3827	43.4156	-2.3536	42.2642	-2.3170	43.6756
-2.5411	43.4962	-2.4911	42.3884	-2.6283	43.8561	-2.5618	43.2964
-2.2890	42.7102	-2.4964	42.5774	-2.4022	41.6106	-2.4042	43.7485

Table 4.2.1
Continued Fraction Coefficients
for the BCC, FCC and HCP
Structures.

These average coefficients are shown in Figure 4.2.1, together with the terminating parameters a_c , b_c^2 obtained with the termination technique developed in Chapter 2.

For reference, we also show the densities of states for BCC and HCP for various numbers of levels, calculated with the terminating parameters from Figure 4.2.1. Figure 4.2.2 demonstrates the relatively rapid convergence of the BCC $n(E)$ towards a form remarkably close to the band structure calculation (Andersen et al. 1977). In Figure 4.2.3 we see that the HCP densities of states are more slowly convergent than the BCC, but still provide a very good representation of the bulk canonical density of states (Andersen et al. 1977).

4.2.2 Structural Energies and Differences.

Rather than working with the band energy, which is large and parabolic, we look directly at the structural dependence by defining the structural energy as

$$U_{\text{struc}}(E) = \int_{-\infty}^E E' n(E') dE' - \int_{-\infty}^E E' n_{\text{skew}}(E') dE' \quad (4.2.5)$$

where $n_{\text{skew}}(E)$ is the density of states of the skew rectangular band fitted to the first four FCC moments (Figure 1.2.4 and equations 2.1.13 and 2.1.14). The first term in equation 4.2.5 is calculated using the coefficients shown in Figures 4.2.1 and 2.2.2, the square root terminator and the terminating parameters

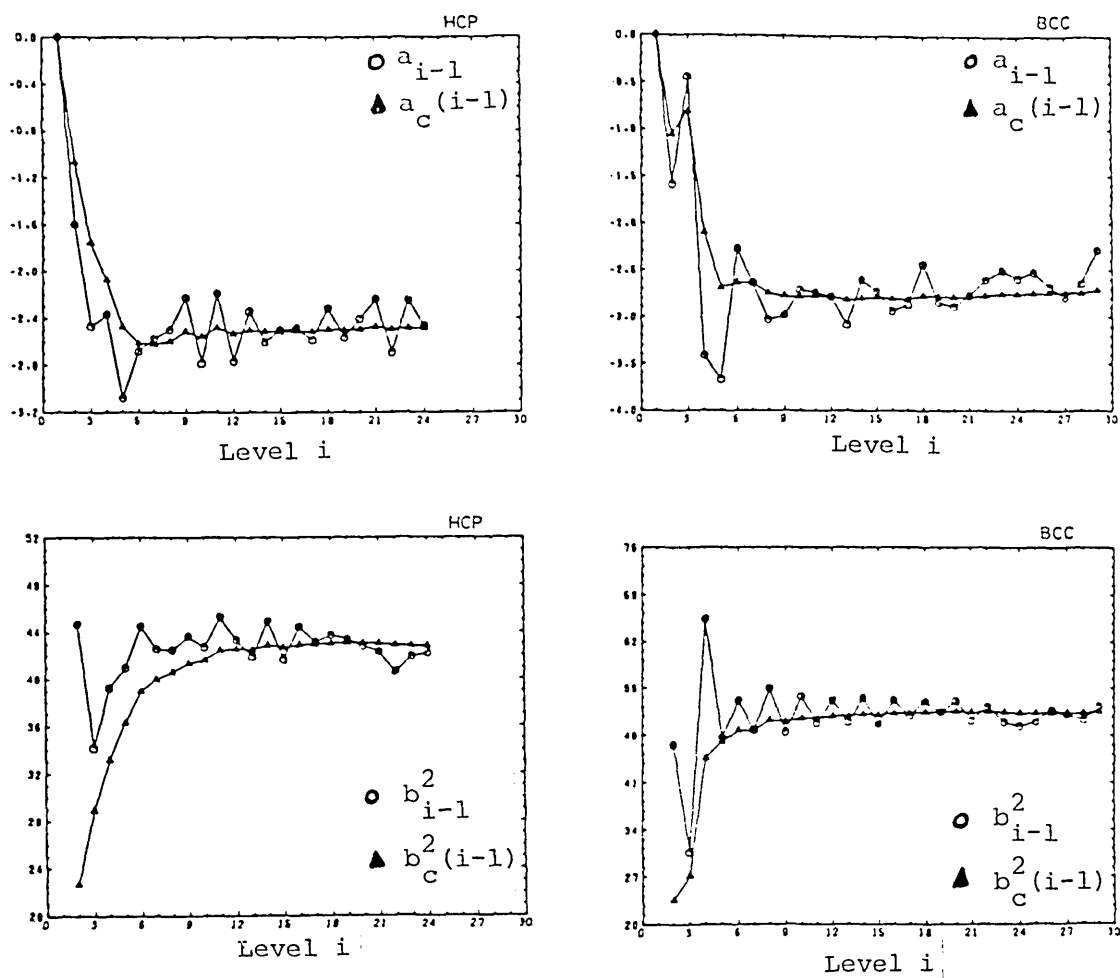


Figure 4.2.1 "Average" coefficients and terminating parameters for the canonical BCC and HCP bands.

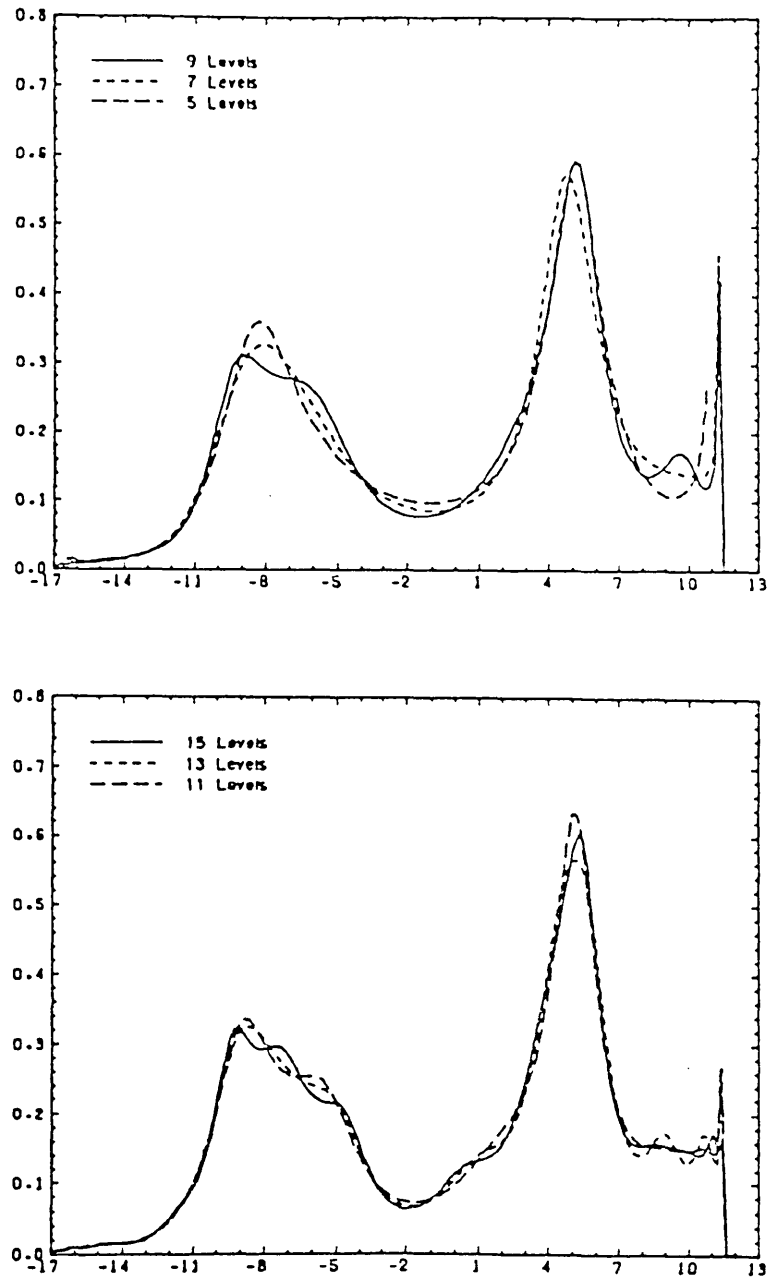


Figure 4.2.2

Convergence of the terminated approximation
to the BCC density of states.

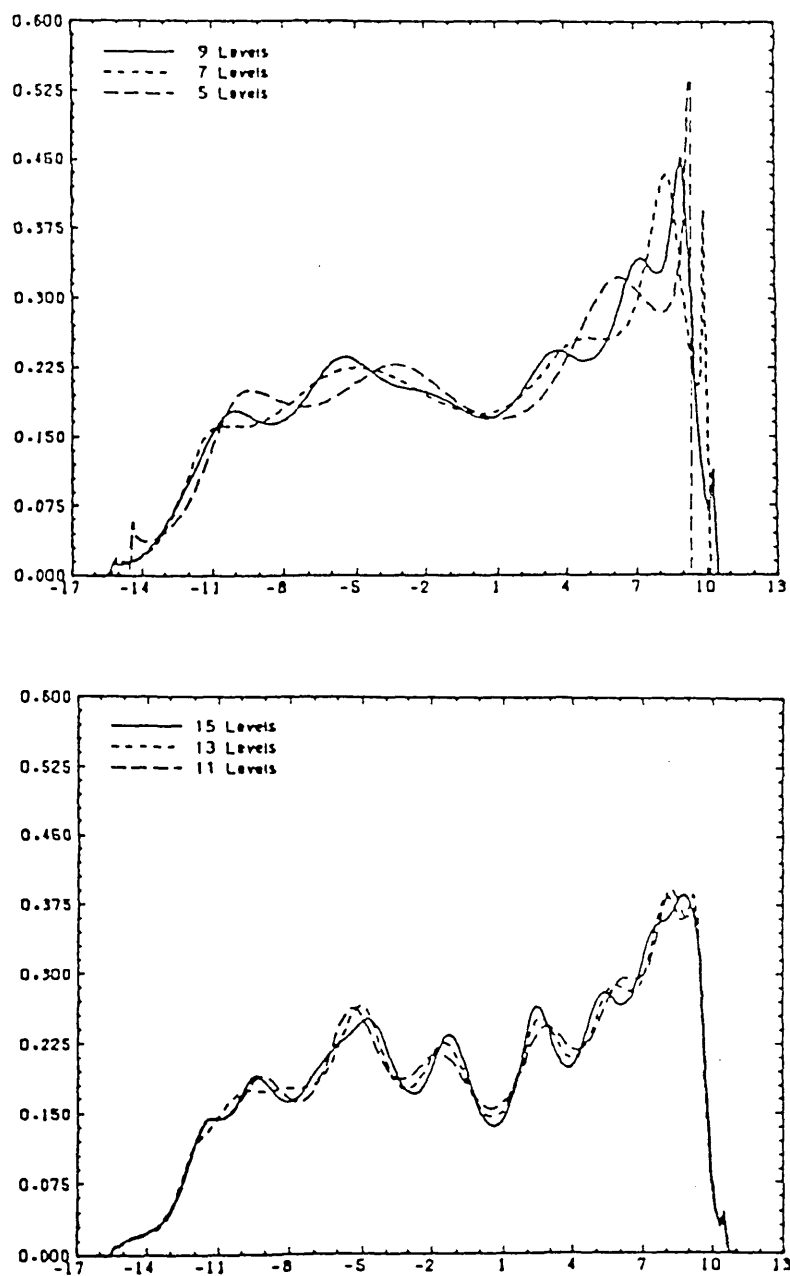


Figure 4.2.3

Convergence of the terminated approximation to the HCP density of states.

calculated according to the technique of Chapter 2. The second term in equation 4.2.5 can be calculated exactly. The resulting $U_{\text{struc}}(N)$ for the three structures is shown in Figure 4.2.4 for various numbers of exact levels. Since the first four HCP moments are identical to the first four FCC moments, the moment theorem (Ducastelle and Cyrot-Lackmann 1971) discussed in section 2.1.3 indicates that the structural energies of both FCC and HCP must have at least two zeroes distinct from the band edges $N = 0$ and $N = 5$. In contrast, BCC has only the first two moments in common with FCC and HCP, and thus there is no requirement for its structural energy to have any zeroes distinct from the band edges. We see from Figure 4.2.4 that these conditions are met.

For two levels, the $U_{\text{struc}}(N)$ for FCC and HCP are identical; and the difference between them is still small for three levels. The p th moment, μ_p , can be written (Cyrot-Lackmann 1967) in terms of closed paths in the tight-binding lattice consisting of p hops. The paths of length 3 that contribute to μ_3 can, at most, extend out to the shell of first nearest neighbours in FCC and HCP, and thus, since the first nearest neighbours are identically placed in these lattices, the moments $\mu_0, \dots, \mu_3$ will be identical. We know, therefore, that, due to the relationship between the moments and the continued fraction coefficients (see section 1.2.4), the first two levels for FCC and HCP will be identical. This may be confirmed by inspection of Table 4.2.1 and is the explanation of the identical $U_{\text{struc}}(N)$ obtained for two levels. Although the μ_4, μ_5 are different in FCC and HCP, due to the differences in the

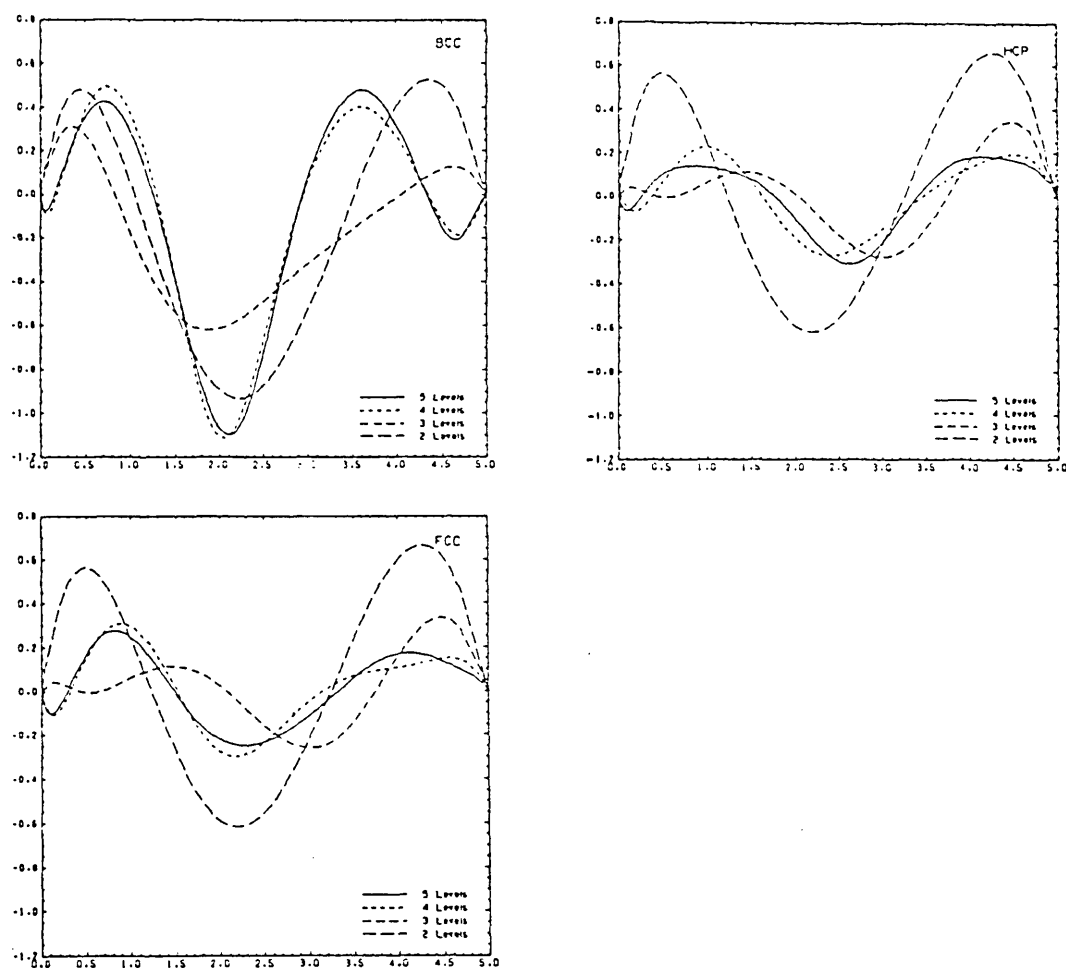


Figure 4.2.4

Structural energies relative to the exact skew rectangular energy for the BCC, FCC and HCP bands.

neighbour environments, we find that the third levels, a_2 , b_2^2 , differ only slightly and give almost indistinguishable $U_{\text{struc}}(N)$. For four levels and beyond, the FCC and HCP coefficients differ significantly and the $U_{\text{struc}}(N)$ reflect this.

The BCC moments, μ_p , differ substantially from the FCC and HCP moments for $p > 2$ due to the qualitatively different nearest neighbour environments, and thus even with only two levels the $U_{\text{struc}}(N)$ for BCC is distinct from the other structures.

We note here that for more than three levels the structural energies calculated are remarkably stable. We will discuss this point in more detail with regard to the structural energy differences below.

In Figure 4.2.5 we present the structural energies as the differences BCC-FCC and HCP-FCC. These Figures are then comparable quantitatively (once both axes are multiplied by a factor of 2) with Figure 3 of Andersen et al. (1977) and qualitatively with the Figures of Pettifor (1970,1972) and Ducastelle and Cyrot-Lackmann (1971). We discuss the significance of these results in the following section, where we conclude the investigation of the structural stability of the pure transition metals.

4.2.3 Discussion.

The structural energies in Figure 4.2.5 compare very well with the calculations of Pettifor (1970,1972) and Andersen et al.

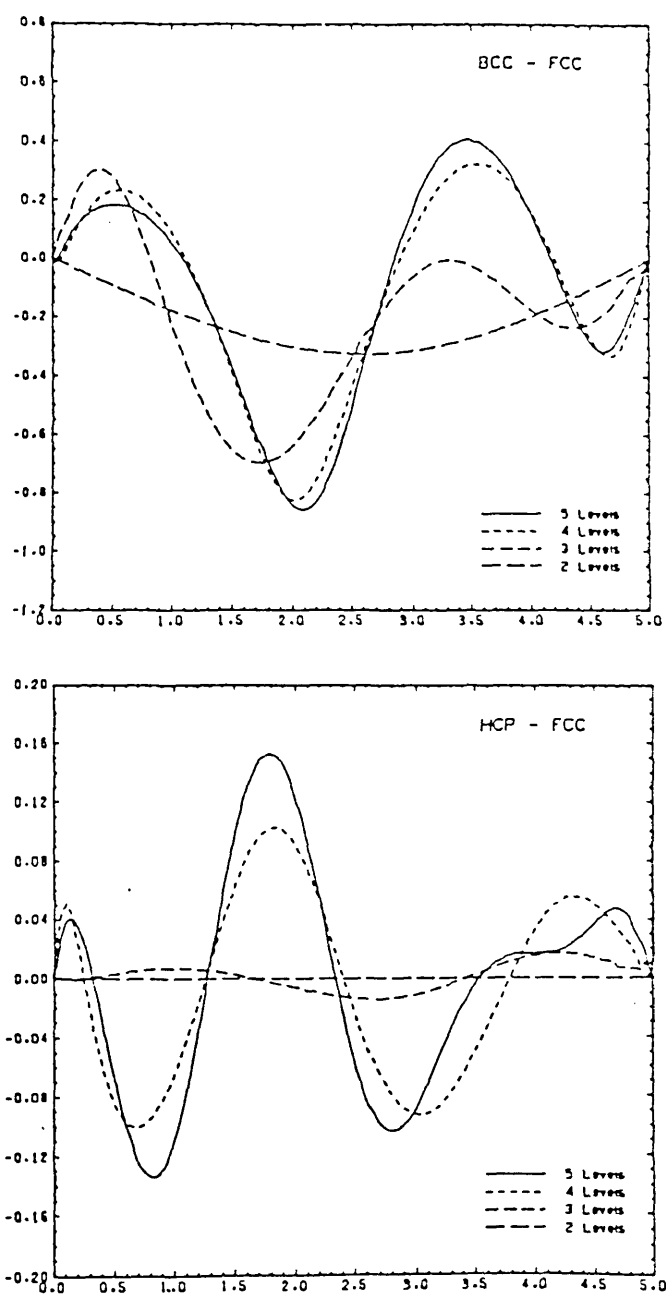


Figure 4.2.5 Structural energy differences between BCC, FCC and HCP.

(1977). Both of these are band structure calculations, and the comparison serves to confirm, once again, our positive expectations of the termination technique. The structural trend HCP - BCC - HCP - FCC across the transition metal series is correctly reproduced although, in common with the band structure calculations, a return to BCC is predicted for the noble metal end of the series.

Although Pettifor (1970,1972) and Andersen et al. (1977) were able to calculate the structural energy differences, because their calculations were band structure-based, they were unable to discuss the origin of the predominant structure of $U_{\text{struc}}(N)$ or to shed any light on which nearest neighbour environments are dominant in determining the structural stability of the transition metal phases. The recursion method, in contrast, is a real space method and, moreover, each successive level in the fraction characterises the effect on the central atom of increasingly distant environments. It is, therefore, ideally suited to approach these questions.

It is clear from Figure 4.2.5 that only the first four levels need be included in the calculation in order to achieve good convergence of the structural energy. For two and three levels the $U_{\text{struc}}(N)$ does not have the correct form, and the use of more than four levels does not greatly change the $U_{\text{struc}}(N)$. Turchi and Ducastelle (1985) have shown very recently that μ_5 (i.e. the third level) is sufficient for the FCC-BCC case (see their Figure 4), provided that a correct, or very nearly correct, b_3 is used. In our calculations, as can be seen from Figure 4.2.1, b_3 is

significantly different from the final asymptotic value; for this reason, we find that four levels are required for convergence.

Contributions to the 4th level come from hopping shells 1-4, from atoms that can be reached from the central atom by a maximum of three nearest neighbour hops. For FCC at 4 levels, 90% of the weight of the recursion orbital is divided approximately equally between shells 3 and 4 (this is reflected in a root mean square extent $R_4 = 2.44$). Also, the 56% of the weight that is on and within shell 3 is distributed over shells 1-3 in approximately the same way as the total weight for level 3. This indicates that in the absence of a drastic redistribution of weight within shells 1-3, the dominant contribution to the FCC structural energy must come from the atoms within the 4th shell. Because of the similarities of the HCP structure to the FCC, this argument also holds for the dominant contribution to the HCP structural energy. In BCC the situation is complicated by the second nearest neighbour hopping. This makes the hopping shells considerably more extended than in the close-packed structures. For four levels, about 50% of the weight of the recursion orbital lies on the 3rd shell and 20% on the 4th ($R_4 = 2.03$), but the weight within 3 shells is distributed in generally similar fashion to 3 levels. It is believed that essentially the same conclusion can be reached as to the dominant contribution to the BCC structural energy. Further insight into the BCC case might be gained by "switching off" the second nearest neighbour interaction.

§4.3 The Transition Metal AB Compounds.

We deal in this section with the structures of the transition metal - transition metal AB compounds. Predictive two-parameter characterisations of compound structures have been much discussed in recent years (see section 4.3.1). We investigate here the power of simple calculations and a two parameter model in the separation of the structures of the transition metal AB compounds.

In section 4.3.1 we discuss the concept of structure maps in general and those proposed for the transition metal compounds in particular. The details of our calculations are set out in section 4.3.2. In section 4.3.3 we present the results of the calculations of the structural energies and construct a theoretical structure map. The success and value of the calculations are then discussed.

4.3.1 Structure Maps.

In the investigation of compound structure, much interest has been shown in structure maps. The hope underlying these is that coordinates characterising the individual components of the compound may be sufficient to unambiguously predict the compound crystal structure. They are essentially a means by which to order data.

A number of different coordinates have been used in attempts to achieve structural separation among compounds. St. John and Bloch (1974) used a quantum defect electronegativity scale for

non-transition metals extracted from the Pauli force model and found good separation of the 59 $A_n B_{8-n}$ non-transition metal compounds. Zunger (1980) used parameters derived from atomic core size to achieve reasonable separation among transition metal compounds. Burdett et al (1981), using the parameters of Zunger, found good separation of the AB_2X_4 spinel structures. Machlin and Loh (1980) constructed a structure map for the transition metal compounds using the valency of the individual components. The structural separation achieved with these coordinates is seductive; Zunger (1980) argued, on the basis of the structural separation achieved with his coordinates derived from the sp characteristics of the atomic components, that the structures of the transition metal compounds are determined primarily by the long range sp electron interactions.

Pettifor (1983) showed that a new "chemical scale" can be constructed which gives near-perfect structural separation for over 500 binary compounds ranging right across the Periodic Table. This scale has no microscopic meaning, but reflects the chemical trends of the elements. A section of this structure map is used to compare our calculated theoretical structure map against.

4.3.2 Computational Details.

In this series of calculations, the six most common transition metal AB compound crystal structures have been used. These are the B2(CsCl), $L1_0$ (CuAu), B11(CuTi), B19(AuCd), B27(FeB) and B33(CrB). The atomic positions used have been taken from Pearson (1958) for the archetypal compounds. The structural energy, $U_{\text{struc}}(N)$, for each compound structure is used to determine the stable crystal structure at each N.

The total energy per atom is given by equation 4.1.3. The difference in total energy, ΔU , which determines the stable crystal structure, is given by

$$\Delta U = U_A(V_A) - U_B(V_B) \quad (4.3.1)$$

where V_A , V_B are the equilibrium volumes of compounds A and B respectively.

A recently proved theorem (Pettifor 1985 J Phys C, to be published) has shown that to first order in $\Delta U/U$ the structural energy difference can be written

$$\Delta U = [\Delta U_{\text{band}}] \Delta U_{\text{rep}} = 0 \quad (4.3.2)$$

i.e. the relative stability is determined by the band energy alone, provided the volumes of the two structures are fixed to show the same repulsive energy. That is:

$$\Delta U = U_{\text{band}}^A(\hat{V}_A) - U_{\text{band}}^B(V_B) \quad (4.3.3)$$

where $\hat{V}_A$ is the prepared volume such that

$$U_{\text{rep}}^A(\hat{V}_A) = U_{\text{rep}}^B(V_B) \quad (4.3.4)$$

This means that we can tackle the problem of calculating structural energies in two steps. Firstly, we set up the volumes of the two compounds so that $\Delta U_{\text{rep}} = 0$; this is equivalent to taking into account the size factor. Then, we compare their bonding at these volumes.

In order to keep the model simple, since we use the canonical hopping parameters which are proportional to R^{-5} , we assume that U_{rep} is proportional to R^{-10} , which gives reasonable bulk properties (see Figure 30 of Pettifor 1983).

The second moment in a tight binding lattice may be written (Ducastelle and Cyrot-Lackmann 1970) as

$$\mu_2 = \sum_{R \neq 0} (dd\sigma_R^2 + 2dd\pi_R^2 + 2dd\delta_R^2) \quad (4.3.5)$$

where the sum is over all nearest neighbours. Since, with canonical hopping parameters, μ_2 will be proportional to R^{-10} , we use $\Delta\mu_2 = 0$ as a measure of $\Delta U_{\text{rep}} = 0$ (see Pettifor and Podloucky 1984). The calculations are therefore performed under the constraint that

$$\Delta\mu_2 = 0 \quad (4.3.6)$$

There should be a difference in the hopping parameters according to the atoms involved. In these calculations, we neglect this difference and use the same values of the hopping parameters

for hopping between all types of atoms. The atomic species in our model are, therefore, differentiated only by their d level energies, E_d . This approximation allows us to focus our attention on the importance of the electronegativity difference (represented here by ΔE_d) and the average number of valence electrons per atom, N .

The reference value of the second moment and the values of the hopping parameters are set by consideration of BCC Niobium at its equilibrium atomic volume with a d bandwidth of 10eV. These are reasonably typical values for the transition metals. Using the value of $a = 3.3 \text{ \AA}$ from Pearson (1958) and the value for the ratio $(S/R)_{\text{BCC}}$ from equation 4.2.2, we can determine the hopping parameters. From these and equation 4.3.5, we can determine the reference second moment.

The clusters used for the recursion calculations were of a few thousand atoms in a simple cubical cluster, sufficient to give about 8 exact levels. For each of the six structures the recursion coefficients were calculated for four values of ΔE_d : 0, 2, 4 and 8 eV. At the greatest d level separation some of the structures exhibited band gaps in their density of states; the terminating parameters for these were calculated using the methods described in Chapter 3. The methods of Chapter 2 were used for those without gaps.

We have used the convention that in the AB compound the electronic occupation of the d bands on atom A is not less than that on atom B; $N_A \geq N_B$. This implies that the d level, E_d , for atom A is lower in energy than the d level for atom B. By definition, therefore, ΔE_d is non-negative.

4.3.3 Results.

The density of states obtained with the appropriate termination technique are shown in Figure 4.3.1, for each structure and each ΔE_d . These graphs show the sum of the $n(E)$ for both A and B components. Also shown for comparison are the skew rectangular density of states which are used as a reference for the calculated $U_{\text{struc}}(N)$, the skewness being determined by the BCC CsCl lattice.

For a given choice of ΔE_d all the densities of states in Figure 4.3.1 have the same second moment μ_2 , where the total second moment, $\mu_2 = \mu_2^A + \mu_2^B$, depends on ΔE_d through

$$\mu_2 = \mu_2^0 + \frac{5}{2} (\Delta E_d)^2 \quad (4.3.7)$$

where

$$\mu_2^0 = 5(b_1^2(A) + b_1^2(B)) \quad (4.3.8)$$

is independent of ΔE_d .

The changes evident in the skew rectangular bands used as reference are thus due to the dependence of μ_2 on ΔE_d as indicated in equation 4.3.7. Note that the skew rectangular band is used as a reference even for those bands exhibiting gaps in their $n(E)$. Comparison of different structures is therefore performed with $\Delta\mu_2 = \Delta\mu_2^0 = 0$ as required by equation 4.3.6.

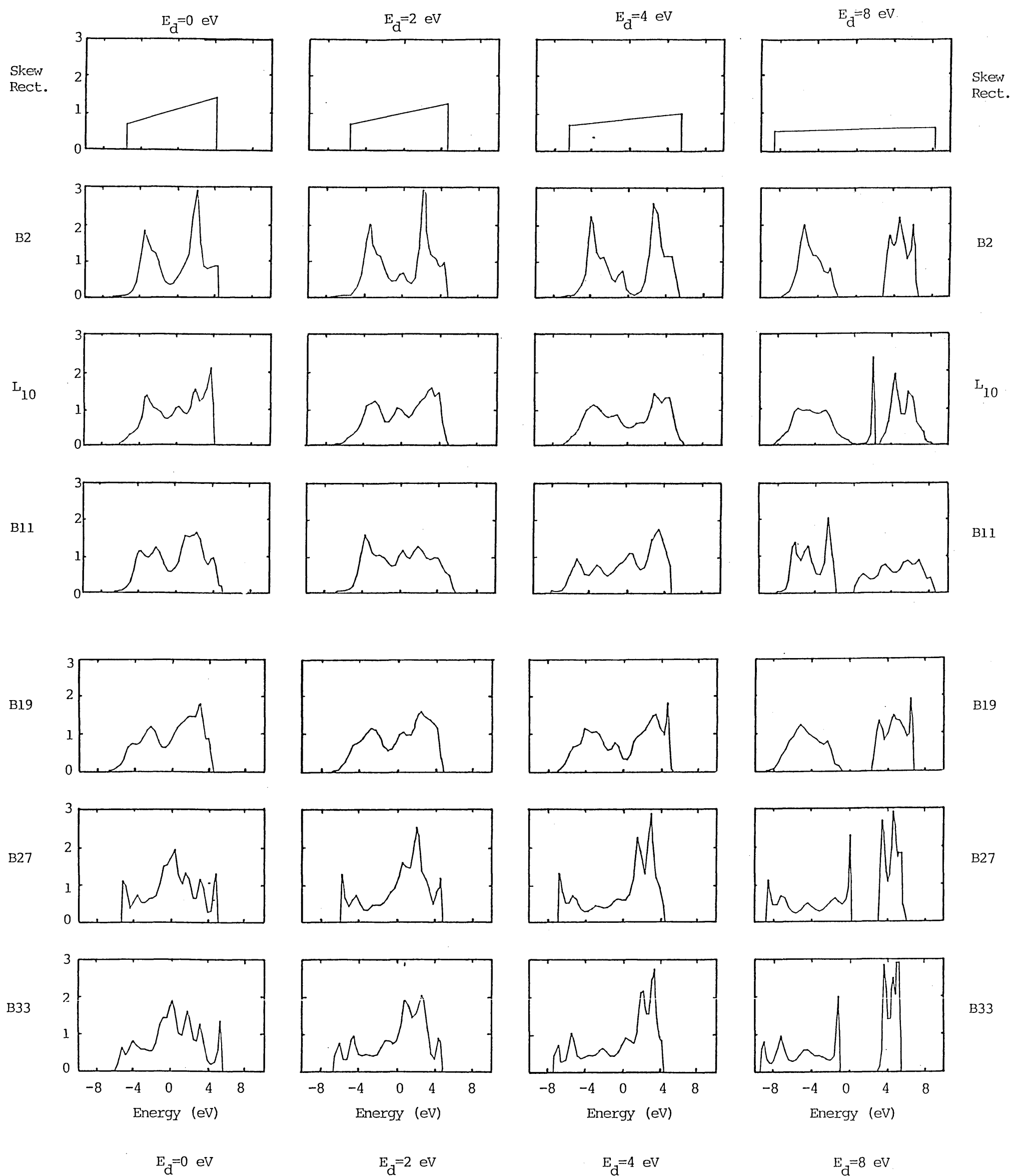


Figure 4.3.1 Densities of States for the AB alloys, calculated with the appropriate termination technique. The skew rectangular band used as a reference for the structural energies is included for comparison.

The number of levels used in the calculations of the density of states shown in Figure 4.3.1 was chosen by examination of the convergence of the structural energies. In Figure 4.3.2 we show the energies, $U_{\text{struc}}(N)$, for each structure at $\Delta E_d = 0$ eV. These energies display a similar behaviour to that seen for the pure transition metals: below a certain number of levels the graphs have a qualitatively incorrect form, while above this number the overall form is stable. Similarly to the pure metals, we find that the critical number of levels is about three. We have chosen 10 levels as a number of levels at which all $U_{\text{struc}}(N)$ are stable and generally well-converged.

We can now draw up a comparison of the $U_{\text{struc}}(N)$ for each structure at a particular ΔE_d . In accordance with our basic assumptions that this d band energy should be sufficient to predict the general structural trends in the transition metal AB compounds, we take as the stable structure for some N the structure which has the smallest (i.e. most negative) $U_{\text{struc}}(N)$. These four graphs, one for each ΔE_d , are shown in Figure 4.3.3. On each we have indicated the ranges of N within which each structure is stable.

The points marked as boundaries between two structures can be transferred to Figure 4.3.4, which is the structure map based on the two parameters, N and ΔE_d . The positions of the broken lines have been obtained by linear interpolation from the structural energies of Figure 4.3.3. This structure map is not effective as a predictive aid, nor can it be easily compared with experimental results. It is not sufficient to use the atomic d level energy for

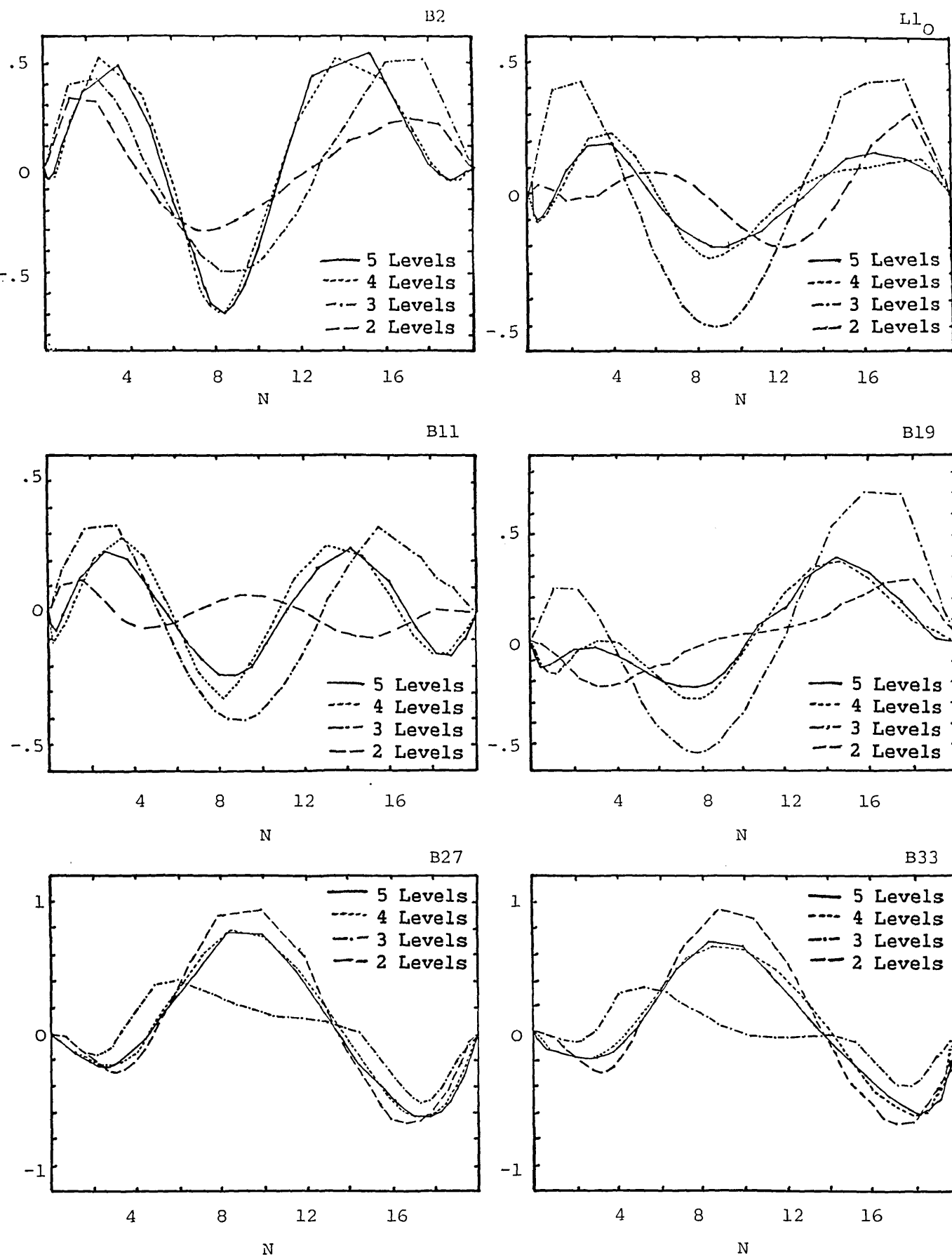


Figure 4.3.2

Convergence of the Structural Energies
 $U_{\text{struc}}(N)$ for the Transition Metal AB Alloys

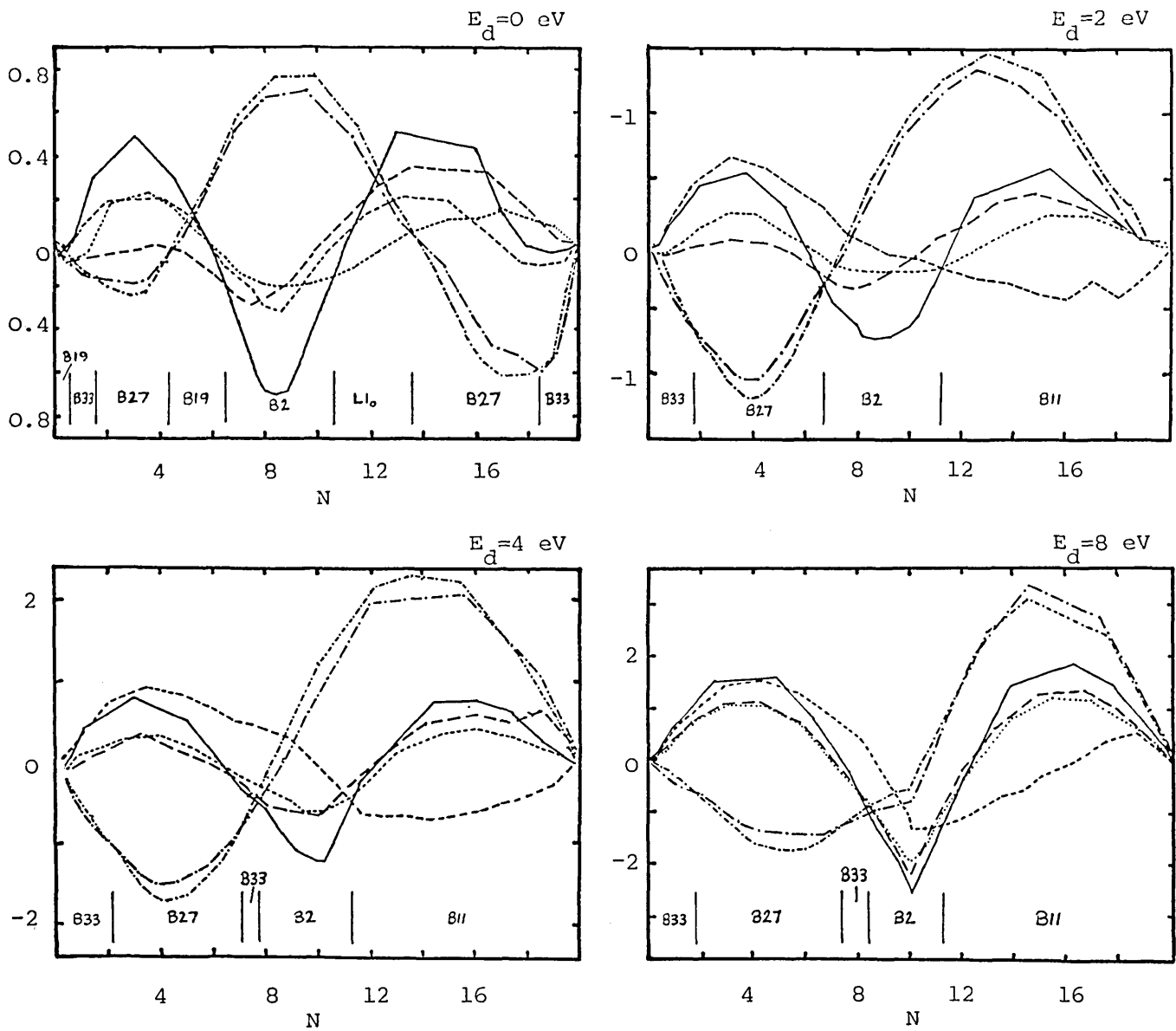


Figure 4.3.3 Structural Energies, $U_{\text{struc}}(N)$, of Transition Metal AB Alloys relative to the skew rectangular energy for $\Delta E_d = 0, 2, 4, 8$ eV

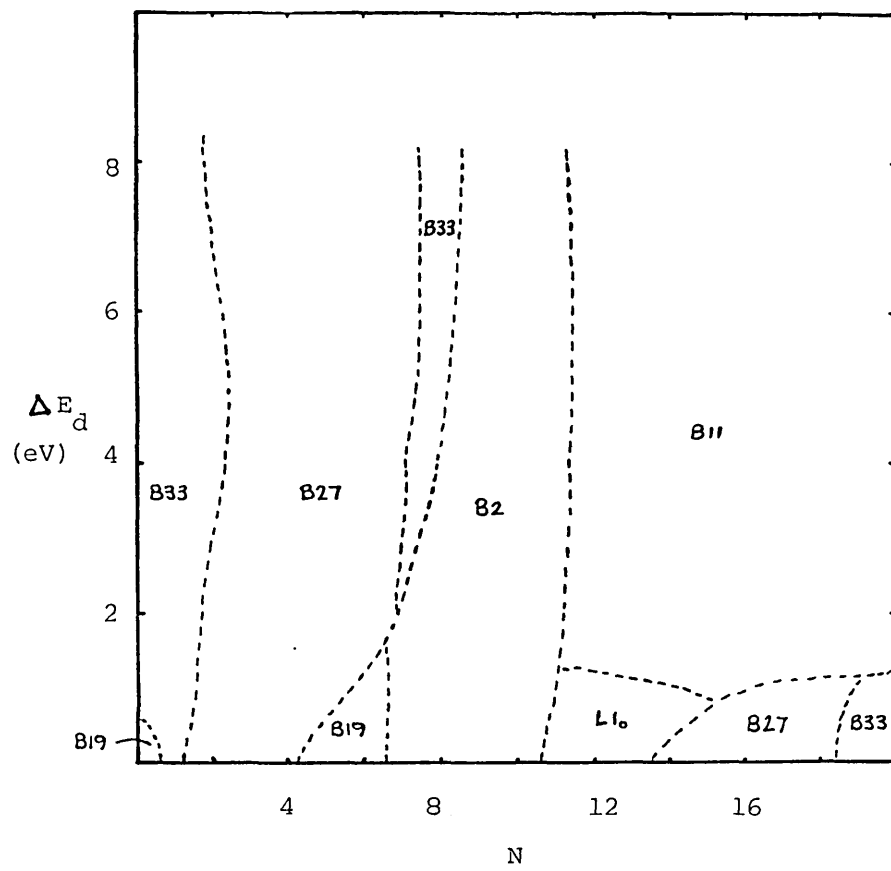


Figure 4.3.4 Theoretical Structure Map for the Transition Metal AB alloys, based on N and ΔE_d

each component to find a ΔE_d as significant renormalisation of the d level energies will occur as a result of charge transfer. The magnitude of the difference in the electronic occupation of one of the components, N_A say, between the pure phase and the compound is smaller than the renormalisation in ΔE_d . For example, in the Y-Co compound discussed in Chapter 5, it is found that the renormalisation of ΔE_d is on the order of 5 eV, while the charge transfer is generally less than 0.5 of an electron.

We have, therefore, constructed a new structure map based on the electronic occupations, N_A , N_B , of each component of the compound with respect to the CsCl lattice. The theoretical structure map constructed in this manner is shown in Figure 4.3.5. Along the diagonal $\Delta E_d = 0$, and along the upper boundary $\Delta E_d = 8$. The phase boundaries, once again based on a linear interpolation from Figure 4.3.3, are shown as full lines, and the appropriate symbol has been used to fill the regions on this plane within which each structure is stable. We compare this structure map with that shown in Figure 4.3.6 for the same structures characterised by Pettifor's chemical scale (Pettifor 1983).

This comparison indicates that our simple calculations capture the overall aspects of the structural separation in the transition metal AB compounds. Within our approximation where atomic species are distinguished only by their d level energies, the B2(CsCl) structure at $\Delta E_d = 0$ is simply BCC. Similarly, L1₀(CuAu) is a slightly distorted FCC structure. The order of these structures along the diagonal $\Delta E_d = 0$ line is in

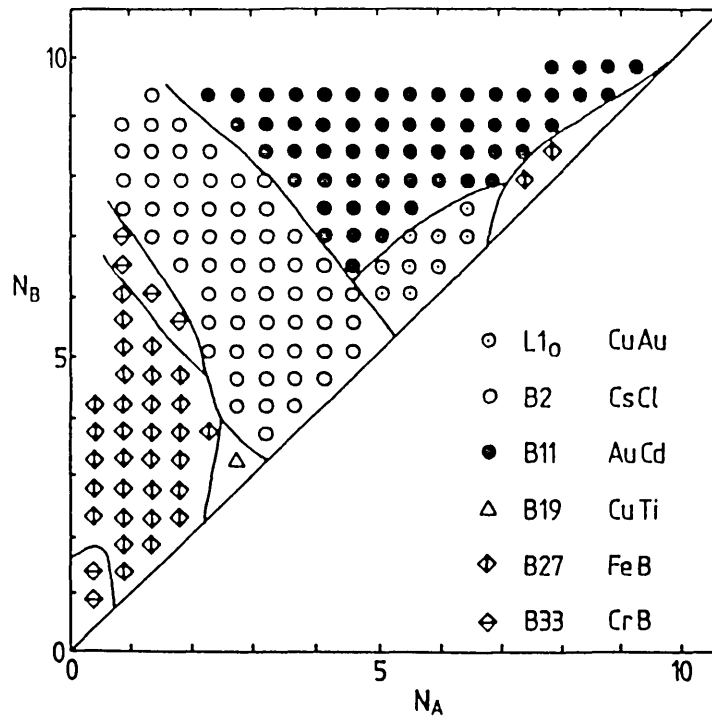


Figure 4.3.5 Theoretical Structure Map of the Transition Metal AB Alloys

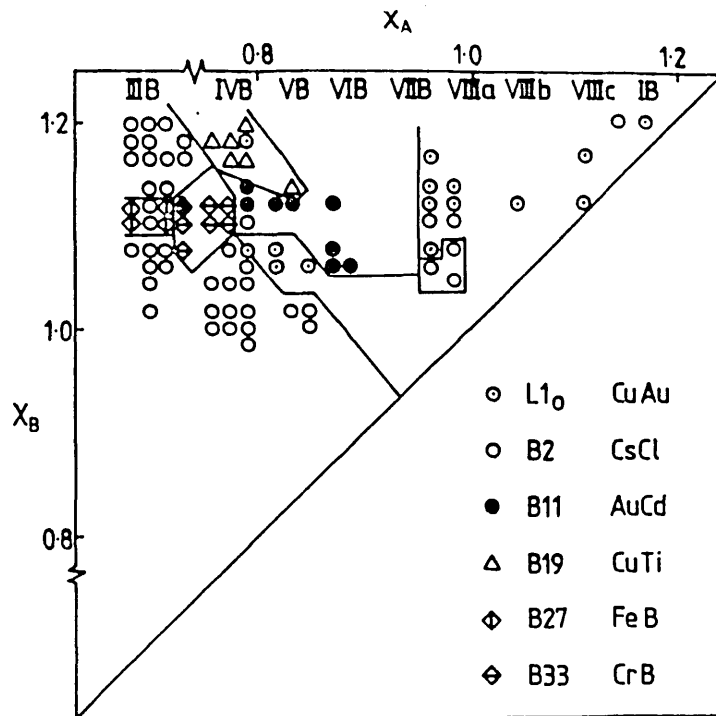


Figure 4.3.6 Experimental Structure Map of the Transition Metal AB Alloys, using Pettifor's Chemical Scale

accordance with the structural separation found in section 4.2 for the pure transition metal BCC and FCC structures, and corresponds to that shown in Figure 4.3.6. The transition, with increasing total number of electrons, N , and increasing ΔE_d , from B2 and Ll_0 to B11 is also reproduced by our calculations. Although the boride phases, B27 and B33, are considerably more extensive in Figure 4.3.5 than in Figure 4.3.6, their order, from B33 to B27 with decreasing N , in the region adjacent to B2 is correct.

The boride structures B27(FeB) and B33(CrB) are shown in Figure 4.3.5 to be exceptionally stable for small N and for large N and small ΔE_d . By reference to Figure 4.3.1, it can be seen that this stability is due to the greater bandwidth in these structures and to the relatively high densities of states near the band edges.

This effect is a reflection of our lack of consideration of atomic relaxation effects. In the borides FeB and CrB, the structure is stabilised by the smallness of the boron atom. In our calculations, we have used the atomic positions for these archetypal compounds and not allowed for any relaxation of the atomic positions caused through the significantly larger transition metal atoms. The atoms on the boron positions in these structures will effectively form chains, while the atoms on the metal positions will be at much greater separations. The high densities of states near the band edges for the B27 and B33 structures in Figure 4.3.1 are reminiscent of the density of states of a chain.

These calculations show that the tight-binding band model captures the essential ingredients governing the structural

stability of compounds. However, it is clear from a comparison of theory and experiment in Figures 4.3.5 and 4.3.6 that much more research is still required for a satisfactory theory of structure. This may be achieved during the next few years by writing the band energy in terms of the nearest neighbour bond contributions as suggested by Finnis and Pettifor (1985, private communication) which would allow a detailed analysis of the structural energy with respect to the different bond contributions and to the role of the local atomic environment.

Chapter 5. Y_4Co_3 .

In this Chapter we discuss in detail the structure and properties of the intermetallic compound known as Y_4Co_3 . In §5.1 we discuss its superconducting and magnetic properties and review the experimental position with regard to their elucidation. In the light of this, we indicate what relevance simple calculations of the electronic structure of this material may have and argue that useful information may be derived about the magnetic properties in particular.

We next discuss, in §5.2, the model used for the compound and the details of the calculational procedure. The results of the calculations are presented and their relation to the behaviour of Y_4Co_3 discussed.

§5.1 The Structure and Properties of Y_4Co_3

Rare-earth-Cobalt intermetallic compounds have been the subject of much investigation (see for example, Buschow 1971,1977 and references therein). A phase at the composition R_4Co_3 has been found for many rare-earth elements, R. The structure of these phases is designated Ho_4Co_3 (Lemaire et al. 1969) and is shown in Figure 5.1.1. Two types of rare-earth sites, R(1) and R(2), make up triangular columns running parallel to the c axis. These columns are constructed from trigonal R prisms centred by two types of Co sites, Co(1) and Co(2). The designation of the R and Co sites as h or d sites is also indicated in Figure 5.1.1. A third site, Co(3) in position b, was found (Lemaire et al. 1969) on the c axis. These sites are within the hexagonal "tube" formed by the R(1) sites of six adjacent columns. This b site has two positions in each unit cell, at $z = 0$ and $z = 1/2$ which were thought to be randomly occupied so as to comply with the stoichiometry. Full occupation of these sites would lead to unusually short Co-Co distances; for example in Ho_4Co_3 , $c/2 \approx 2\text{\AA}$. The Y-Co compound at about 43 atomic percent Co was thought to be Y_4Co_3 in this Ho_4Co_3 structure, with the lattice parameters $a = 11.527\text{\AA}$, $c = 4.052\text{\AA}$.

Berthet-Colominas et al. (1968) discovered that the compound Y_4Co_3 displays a weak spontaneous magnetisation of $0.11\mu_B$ per formula unit at liquid helium temperatures with an ordering temperature of 13K. This result was unexpected since, as will be discussed later, the neighbouring Y-Co phases exhibit no spontaneous magnetisation.

A recent detailed investigation (Grover et al. 1982) of the Y-Co phase diagram in the region 25% Co to 50% Co has revealed stable phases

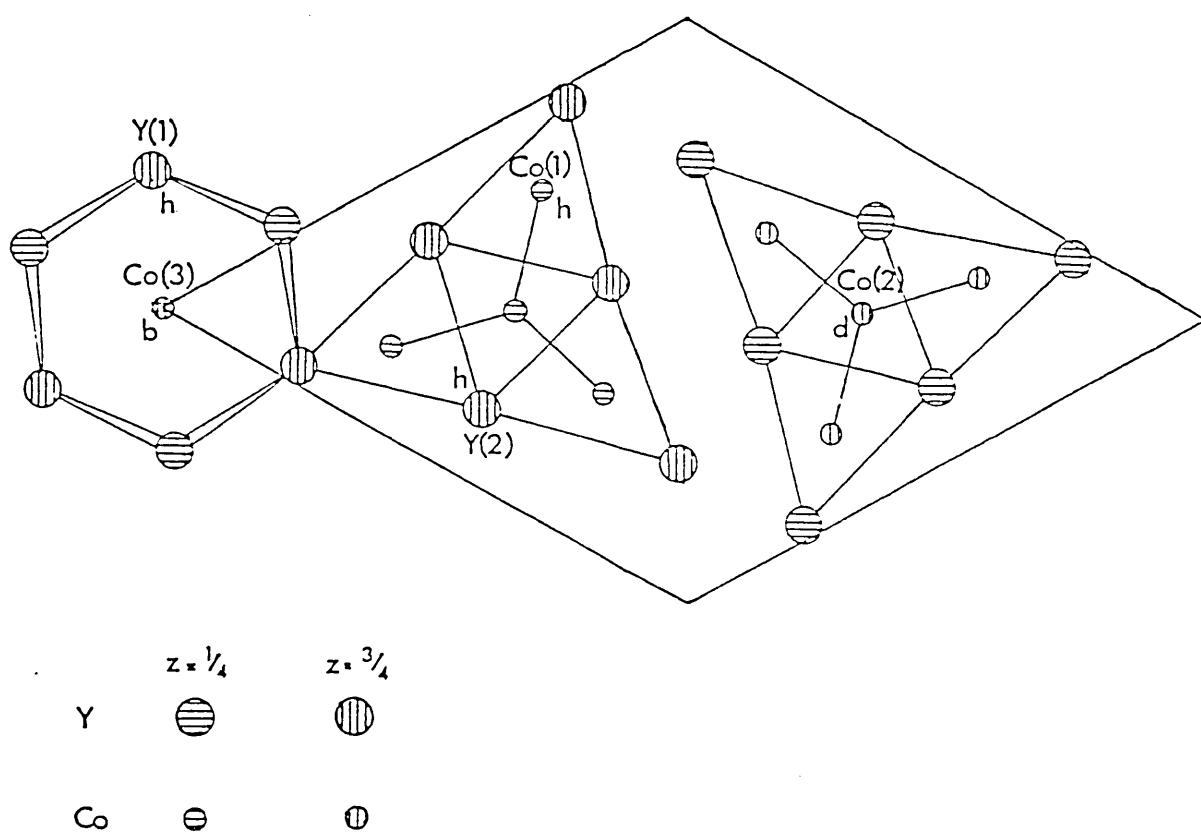


Figure S.1.1 The Ho_4Co_3 Structure.

at Y_8Co_5 , Y_9Co_7 , YCo and a metastable phase at Y_3Co_2 ; no phase was found at the composition Y_4Co_3 . It was suggested that the structure of Y_9Co_7 is that proposed (Berthet-Colominas et al. 1968) for the phase thought to be Y_4Co_3 , but with four Co(3) atoms on the c axis of three vertically stacked unit cells. An arrangement suggested for these Co(3) atoms has three separated by $2.5\text{\AA}$, with the central Co(3) lying at one of the $z = 0, 1/2$ sites suggested for Y_4Co_3 (Berthet-Colominas et al. 1968), and the fourth relatively isolated at a Co-Co distance of about $3.5\text{\AA}$. This, it is suggested, could be an attractive site for the formation of a local moment.

The results of recent X-ray studies (Yvon et al. 1983) on a small single crystal of Y_9Co_7 conflict with the proposed structure of Grover et al... This study confirms the basic hexagonal Y_4Co_3 structure but did not find the suggested ordered c axis arrangement. Instead, an almost constant column of electron density was found running along the c axis within the "tube" formed by the Y(1) atoms. This feature proved not to be caused by small static or dynamic displacements of the Co(3) atoms. Their failure to find any superstructure reflections led Yvon et al. to conclude that the three dimensionally ordered structure proposed by Grover et al. (1982) is incorrect. They propose instead that the c axis Co chains are individually two dimensionally ordered, but have little or no correlation with the Y "tubes" in which they lie. This one dimensional disorder between the chains, they suggest, may lead to planes of diffuse X-ray intensity which may not have been observed due to the small size of their sample. This X-ray study is thus unable to shed much light on the crucial matter of the c axis arrangement.

The uncertainty with regard to the structure is important in

discussions of the properties of Y_9Co_7 . The original work of Berthet-Colominas et al. (1968) on Y_4Co_3 revealed a very weak spontaneous magnetisation of $0.11\mu_B$ per formula unit, with a Curie temperature of 13K. A subsequent study by Gratz et al. (1980) of the magnetic and electrical properties of Y_9Co_7 confirmed the magnetic ordering with a revised value of 8K for the Curie temperature. It was found that the reciprocal magnetic susceptibility as a function of temperature has a pronounced curvature towards the temperature axis, which is fitted very well by the relation

$$\chi(T) = \frac{C}{(T - \theta)} + \chi_0 \quad (5.1.1)$$

Gratz et al. (1980) point out that an expression of this form can be derived from the work of Bloch and Lemaire (1970). The first term in (5.1.1) describes the temperature dependence of the susceptibility of a system of localised moments and the second, temperature independent term is derived from an itinerant band. The curvature of the Arrott plots (σ^2 against H/σ , σ = magnetisation, H = applied field) were also said to imply the coexistence of localised magnetic moments and an itinerant d band. This study offers the following explanation for the properties of Y_9Co_7 : localised Co moments coexist with an exchange split itinerant d band whose Fermi level is thought to lie close to a maximum in the density of states, much like the situation in YCo_2 (Cyrot and Lavagna 1979). The Co site favoured by Gratz et al. for the local magnetic moment was the c axis b site.

A nuclear magnetic resonance study of Y_4Co_3 , however, led Figiel et al. (1981) to a conflicting conclusion as to the location in the lattice of the local moment. Their interpretation of the NMR data led

them to propose that the Co(2) d site, at the centre of the Y prisms, has a local magnetic moment of $0.12\mu_B$, about four times larger than a moment of $0.03\mu_B$ on the Co(3) b site. Figiel et al. feel, therefore, that the Co(2) d site moment determines the magnetic properties of Y_4Co_3 .

The relationship of the properties of Y_4Co_3 and its structure became even more interesting with the announcement (Kolodziejczyk et al. 1980) that an apparently single phase specimen of Y_4Co_3 showed a transition to a superconducting phase below about 1.5K to 2.0K. The absence of a true divergence in the susceptibility reported indicates that the magnetic order is not so long range as previously thought by Gratz et al. (1980), and the measurements gave an ordering temperature of about 5K. This observation was the first of a transition metal alloy displaying both superconductivity and magnetic order. Although investigation seemed to indicate that their sample was single phase, Kolodziejczyk et al. admit the possibility that the specimen in fact contained a magnetic phase and a superconductive phase. They argue, though, that the neighbouring phases to Y_4Co_3 are insufficiently magnetic for a small admixture to give the magnetic behaviour found in their sample.

Further work (Sarkissian et al. 1981 and reported at a meeting at Imperial College, March 1982 (Wohlfarth 1982)) seems to imply that the two phenomena of superconductivity and magnetism coexist below about 5K, with the former dominating at lower temperatures. The location of the local Co moments, whose existence is well established (see above and Cheng et al. 1982), is therefore of crucial importance. The superconductivity appears to be associated with Y d electrons, as indicated by the rapid suppression of the superconducting transition

temperature by substitution of Gd for Y (Sarkissian et al. 1981). It would thus seem unlikely that the phenomena could coexist if the Co(2) d site supports a relatively strong local moment as reported by Figiel et al. (1981). The proposal by Grover et al. (1982) and Sarkissian et al. (1981) that in the Y_9Co_7 lattice a particular arrangement of Co atoms along the c axis could lead to the formation of a local moment on one of these sites seems more reasonable. It may be possible that the Co d electrons contributing to the local moment at the c axis site are decoupled from those Y d electrons involved in the superconductivity. This controversy over the local Co moment position must, therefore, be settled. Also requiring further work, particularly in the light of the results of Yvon et al. (1983), is the elucidation of the c axis structure. Neutron studies are at present in progress (Grover et al. 1982).

5.2 Theoretical Calculations of the Electronic Structure of Y_4Co_3

The properties of " Y_4Co_3 " discussed in the previous section make it an interesting compound for study by theoretical means. Calculation of the band structure and densities of states may shed some light on the reasons for its peculiar properties, although the lack of experimental agreement on the exact nature and structure of the phase occurring near Y_4Co_3 hampers straightforward calculations. Calculation of bandstructures for the two structures suggested by Grover et al (1982) and Yvon et al (1983) might be able to investigate the implications of each proposed structure on, particularly, the magnetic properties. This would, however, constitute a formidable calculational task - in this section we discuss simple calculations of the densities of states for the Ho_4Co_3 structure (Berthet-Colominas et al 1968).

The complexity of the Ho_4Co_3 structure shown in Figure 5.1.1, with eleven distinct atomic positions, implies that reciprocal space bandstructure calculations will be extremely unwieldy. A bandstructure of 110 exchange-split d bands in a complex Brillouin zone would result. The real space recursion method, however, allows relatively simple calculations of the densities of states to be made. With the termination technique demonstrated in Chapters 2 and 3 of this thesis we may have confidence in extracting values for the densities of states at the Fermi energy. A local Stoner criterion can be used to provide an

indication of the likelihood of local magnetic moments at each atom.

A lattice of some 9300 atoms was constructed, a tetragonal prism in overall shape. The presence of some relatively long nearest neighbour distances in the lattice means that only five levels of the resulting recursion coefficients are exact. In contrast, however, to the work discussed in the early part of Chapter 4, where there were no atoms additional to those required to give exact levels of the recursion coefficients, there are a substantial number of additional atoms. This ensures that the levels beyond the five exact are relatively good approximations. In support of this, we show in Figure 5.2.1 the r.m.s. extent of the recursion orbital at each level. This Figure should be compared with Figure 2.3.2 which shows the r.m.s. extent of the recursion orbital for various FCC cluster sizes. In the latter cases, the significant flattening beyond the number of exact levels is a result of there being no atoms additional to the number required for exact levels - the recursion coefficients, therefore, quickly become inexact. In contrast, the r.m.s. extent of the orbitals for Y_4Co_3 does not show any significant flattening beyond the five levels, indicating that up to, say, ten levels are relatively good approximations.

Once the lattice is established, the parameters we require for the calculation are the hopping parameters $dd\sigma$, $dd\pi$, $dd\delta$ and the d level energies at each atom. We have again used the canonical form of the hopping parameters, in which the nearest neighbour distance for each particular interacting pair of atoms is used. The

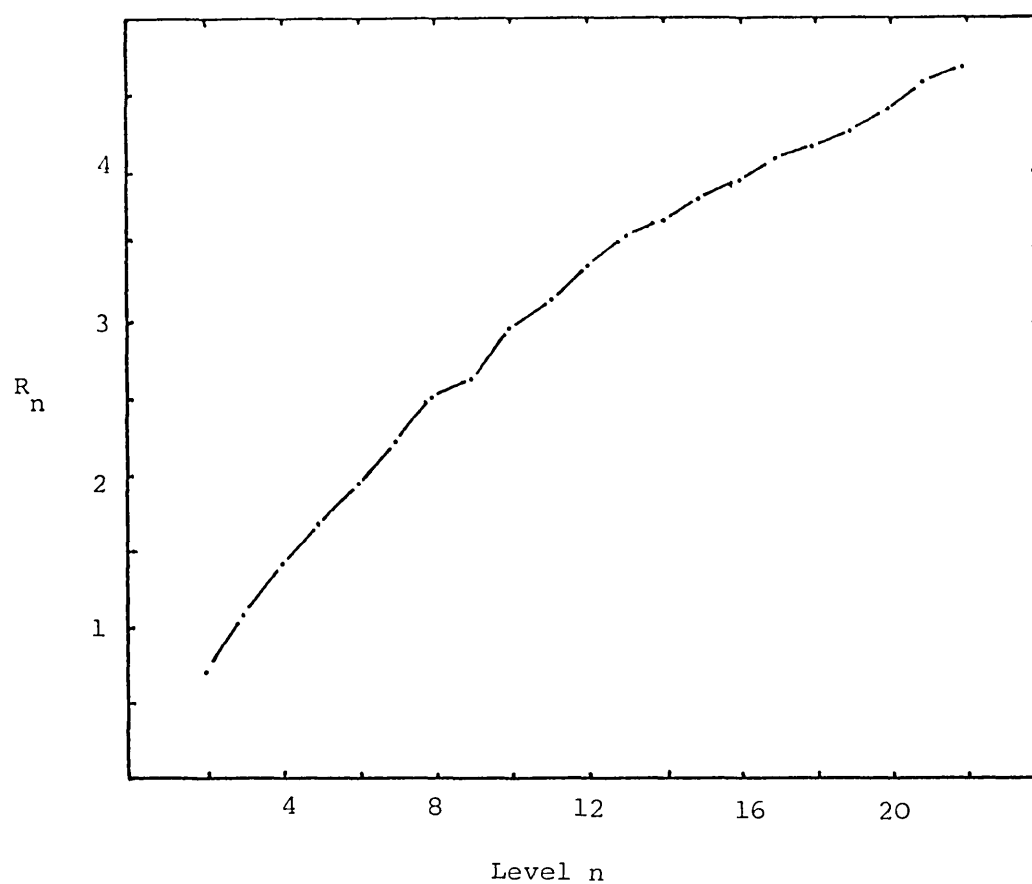


Figure 5.2.1

R.M.S. extent, R_n , of the recursion orbitals for $Y_4CO_3^n$

width of the d band, W_d , and the Wigner-Seitz radius, S , have been taken from Moruzzi et al (1978) and have the following values:

$$\begin{array}{ll} \text{Co: } W_d = 4.964 \text{ eV} & \text{Y: } W_d = 6.283 \text{ eV} \\ S = 1.4019 \text{ \AA} & S = 1.9838 \text{ \AA} \end{array} \quad (5.2.1)$$

The Y-Co hopping parameters are taken as the geometric mean of Y-Y and Co-Co parameters.

The position of the free atom d level energy, E_d^0 , has been interpolated from the values in Herman and Skillman (1968) for the 3d and 4d elements in the $d^{n+1}s^1$ configuration. These are more realistic electronic configurations than $d^n s^2$. The value of E_d^0 is not, however, crucial since the calculations have taken charge transfer into account by modifying the d level energy according to

$$\Delta E_d = \Delta E_d^0 + UQ \quad (5.2.2)$$

where Q is the charge transfer to an atom and U is the interatomic Coulomb integral. We have used a reasonable value for U as 4 eV (see for example Van der Rest et al 1975).

In order to take charge transfer into account, a number of iterations of the calculation are required. A set of charge transfers to each atom (zero initially) are used to modify the d level energies. The recursion coefficients are calculated for each distinct atomic position. These coefficients are then used to

calculate the Fermi energy from the total integrated density of states for all atoms in the unit cell. Finally, the Fermi energy thus derived is projected back onto the individual atom integrated density of states to determine a new set of charge transfers. After nine iterations it was found that the input and output charge transfers differed by less than 0.01 electrons.

Table 5.2.1 shows the self-consistent values of the charge transfer and the density of states at the Fermi energy for each of the non-equivalent atomic sites. The atomic positions are indicated in coordinates relative to the Y_4Co_3 unit cell.

The densities of states for each of the non-equivalent sites are shown in Figure 5.2.2. On each, the position of the Fermi energy is marked and the value of the density of states at the Fermi energy is tabulated in Table 5.2.1.

With a value for I of 1 eV (Gunnarson (1976)), it can be seen from Table 5.2.1 that none of the Co sites exceeds the local Stoner criterion

$$In(E_F) = 1 \quad (5.2.3)$$

On the basis of this simple criterion, we would not, therefore, expect any Co site to display a local magnetic moment.

However, two of the Co(1) sites and the Co(2) site, that is the Co d and h sites in Figure 5.1.1, are extremely close to the criterion, while the the third Co(1) site and the Co(3) site are considerably less close. Local magnetic fluctuations might,

	x	y	z	Q	$n(E_F)$
Y(1)	0.225	0.246	0.250	-0.24	0.70
Y(1)	0.246	0.021	0.750	-0.15	1.78
Y(1)	0.979	0.225	0.750	-0.19	1.09
Y(2)	0.136	0.515	0.250	-0.25	0.86
Y(2)	0.515	0.379	0.750	-0.27	0.92
Y(2)	0.621	0.136	0.750	-0.21	0.72
Co(1)	0.843	0.284	0.250	0.31	0.97
Co(1)	0.284	0.441	0.750	0.24	0.66
Co(1)	0.441	0.157	0.250	0.33	0.92
Co(2)	0.667	0.333	0.250	0.27	0.96
Co(3)	0.000	0.000	0.000	0.33	0.53

Table 5.2.1 Self-consistent charge transfers and density of states at the Fermi energy for each non-equivalent atomic site in the Y_4Co_3 lattice.

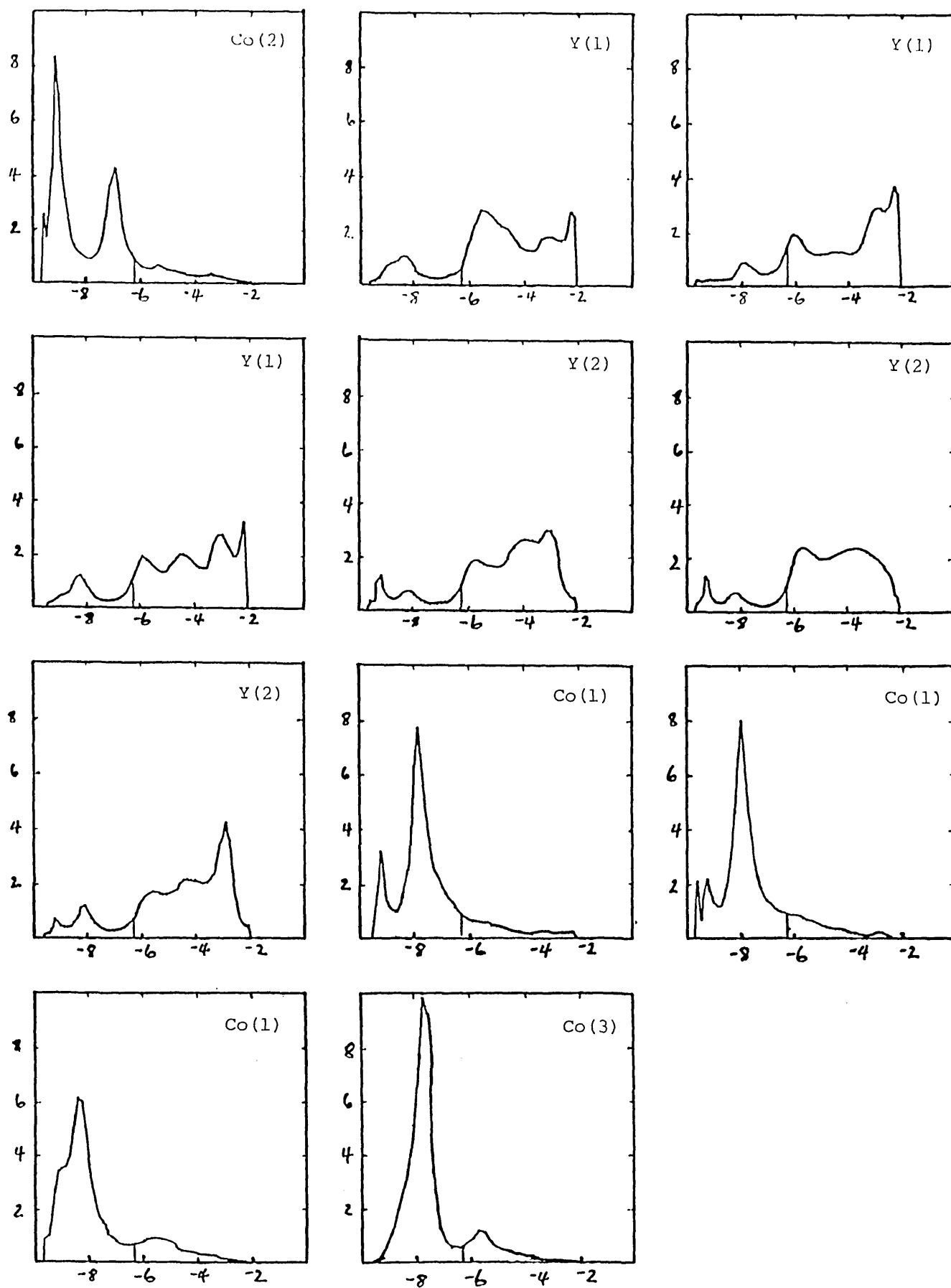


Figure 5.2.2

Density of States for each non-equivalent atomic site in the Y_4Co_3 lattice.

therefore, give rise to a stable, though weak, magnetic moment based around the Co(2), or d, site. This result would appear to support the experimental results of Figiel et al (1981). In addition, the Fermi level lies in a minimum of the Y_4Co_3 density of states - the sum of the individual $n(E)$ in Figure 5.2.2 - which should be compared with the arguments of Gratz et al (1980) following equation (5.1.1).

The simplicity of the calculations must, however, be borne in mind. Whilst the absolute accuracy of the results reported in Table 5.2.1 should be viewed with caution, due to the tight-binding approximation used and the simple termination adopted for the recursion calculations, we might expect the relative closeness of each site to the Stoner criterion to be preserved. The most important assumption underlying the calculations, however, is the structure of the lattice used. In the absence of definitive guidance, we have used for calculational simplicity the Ho_4Co_3 structure shown in Figure 5.1.1. The structural investigations discussed in section 5.1 indicate that " Y_4Co_3 " may well have a more complex structure.

In particular, the $\underline{c}$ axis ordering suggested by Grover et al (1982) for Y_9Co_7 would merit a comparative calculation. The density of states at the central Co site along the $\underline{c}$ axis would resemble a virtual bound state split by the interactions with its Co neighbours in the chain by the order of $dd\sigma$. This form of $n(E)$ increases the possibility of a high value of $n(E_F)$ at this atom, and therefore the possibility of a local magnetic moment.

In summary, the calculations reported here indicate that in a Ho_4Co_3 lattice the most likely site for a magnetic moment is the Co(2), or d, site. Further real space calculations for the proposed structures will prove valuable in the elucidation of the magnetic properties of " Y_4Co_3 ".

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Appendix. The Computer Routines.

In this Appendix we give listings of the most important of the computer routines developed during the course of the research reported in this thesis.

The routines were written originally in FORTRAN IV but parts have been updated to FORTRAN 77. They will all run under the Minnesota FORTRAN compiler, MNF.

The routines are:

FUNCTION DOS : two versions of this routine have been listed, one for the connected band and one for the single band gap - they differ only slightly. This function calculates the density of states at energy E from the continued fraction representation. It requires the coefficients and a supporting subroutine which calculates the value (complex) of the terminator at this energy.

SUBROUTINE TERMFN : two versions of this routine are included. This subroutine calculates the real and imaginary parts of the terminator at energy E . To do so it requires as input the terminating parameters for either the connected band or the single band gap. These parameters are passed in through common blocks, explicitly in the case of the single band gap and as part of the coefficient arrays in the case of the connected band.

SUBROUTINE TERM : This subroutine determines the terminating parameters for the connected band by the methods described in Chapter 2. It requires an external FUNCTION FN to calculate the difference between the moduli of the maximum and minimum eigenvalues. This function must diagonalise the tridiagonal matrices found at the top and bottom band edges, and, as listed, uses a routine from the Numerical Algorithms Group library to do so.

PROGRAM GAPTDTI : This program determines the terminating parameters for the single gap band by the methods described in Chapter 3. This calculation must be implemented as a program rather than a subroutine because the methods are not automatic. The program as written is interactive and relatively easy to use. It is heavily documented.

FUNCTION DOS(E)

(single gap band)

```

C
FUNCTION DOS(E)
COMMON /CFS/ A(50,5),B2(50,5),NL,NC,NQ,IM
COMPLEX EC,T,S
EXTERNAL SQRT,AIMAG

PI=3.14159265
EIM=1.0E-05
EC=CMPLX(E,EIM)
CALL TERMFN(E,RET,AIMT)
T=CMPLX(RET,AIMT)
2 S=EC-CMPLX(A(NL,NQ),0.0)-T
NL1=NL-1
DO 3 I=1,NL1
  M=NL-I
  S=EC-CMPLX(A(M,NQ),0.0)-CMPLX(B2(M+1,NQ),0.0)/S
3 CONTINUE
S=CMPLX(B2(1,NQ),0.0)/S
DS=-AIMAG(S)/PI
IF (IM.GT.0) THEN
  DO 4 I=1,IM
    DS=DS*E
4 CONTINUE
ENDIF
DOS=DS
RETURN
END

```

SUBROUTINE TERMFN(E,RET,AIMT)

(single gap band)

C

```

SUBROUTINE TERMFN(E,RET,AIMT)
COMMON /GAP/ RA,W,GS,GC,A1,A2,E1,E2,E3,E4
COMMON /CFS/ A(50,5),B2(50,5),NL,NC,NSET1,IM
EXTERNAL ABS

NQ=NSET1
T1=2.0*(E+A1+A(NL+1,NQ))*B2(NL+1,NQ)
T2=E*(E+A1)+A2+2.0*B2(NL+1,NQ)
X=(E-E1)*(E-E2)*(E-E3)*(E-E4)
IF (X.GE.0.0) THEN
  AIMT=0.0
  XF=1.0
  IF (E.LE.E3.AND.E.GE.E2) XF=-1.0
  T2=T2+SQRT(X)*XF
  RET=T1/T2
  IF (ABS(RET).LT.1.0E-20) RET=SIGN(1.0E-20,RET)
ELSE
  X=-X
  T3=T2*T2+X
  XF=1.0
  IF (E.LT.E4.AND.E.GT.E3) XF=-1.0
  RET=T1*T2/T3
  AIMT=T1*XF*SQRT(X)/T3
ENDIF
RETURN
END

```

FUNCTION DOS(E)

(connected band)

```

C
FUNCTION DOS(E)
COMMON /CF/ A(35,2),B2(35,2),NL,NC,NQ,IMOM
COMPLEX EC,T,S
EXTERNAL SQRT

PI=3.14159265
EC=CMPLX(E,0.0)
CALL TERMFN(E,RET,AIMT)
T=CMPLX(RET,AIMT)
2 S=EC-CMPLX(A(NL,NQ),0.0)-0.5*T
NL1=NL-1
DO 3 I=1,NL1
    M=NL-I
    S=EC-CMPLX(A(M,NQ),0.0)-CMPLX(B2(M+1,NQ),0.0)/S
3 CONTINUE
S=CMPLX(B2(1,NQ),0.0)/S
DOS=AIMAG(S)/PI
IF (IMOM.GT.0) THEN
    DO 4 I=1,IM
        DOS=DOS*E
4    CONTINUE
ENDIF
DOS=DS
RETURN
END

```

SUBROUTINE TERMFN(E,RET,AIMT)

(connected band)

```

SUBROUTINE TERMFN(E,RET,AIMT)
COMMON /CF/ A(35,2),B2(35,2),NL,NC,NQ,IMOM
C
  AINF=A(NC,NQ)
  BINF=SQRT(B2(NC,NQ))
  EB=AINF-2.0*BINF
  ET=AINF+2.0*BINF
  IF (E.LT.EB.OR.E.GT.ET) GOTO 1
  X=(E-EB)*(E-ET)
  IF (X.GT.0.0) GOTO 1
    AIMT=SQRT(-X)
    RET=E-AINF
    RETURN
1 CONTINUE
  RET=1.0
  AIMT=0.0
  RETURN
END

```

SUBROUTINE TERM(AINF,BINF,B2INF)

(connected band)

```

SUBROUTINE TERM(AINF,BINF,B2INF)
COMMON /ZLT/ AZ(35),BZ(35),B2Z(35),NLZ
COMMON /BOU/ E1,E,BT(2)
EXTERNAL FN
C
E1=1.0E-04
E=X02AAF(E1)
DO 1 I=1,NLZ
  BZ(I)=SQRT(B2Z(I))*0.5
  B2Z(I)=0.25*B2Z(I)
1 CONTINUE
B2Z(NLZ)=2.0*B2Z(NLZ)
BZ(NLZ)=BZ(NLZ)*SQRT(2.0)
AL=AZ(1)
AU=AZ(1)
DO 2 I=2,NLZ
  AL=AMIN1(AL,AZ(I))
  AU=AMAX1(AU,AZ(I))
2 CONTINUE
EPS=5.0E-06
IFAIL=0
CALL C05ABF(AL,AU,EPS,FN,AINF,IFAIL)
IF (IFAIL) 1000,3,1000
3 DUM=FN(AINF)
BINF=0.5*(ABS(BT(1))+BT(2))
B2INF=BINF*BINF
RETURN
1000 STOP
END
C
C
C
FUNCTION FN(AINF)
COMMON /ZLT/ AZ(35),BZ(35),B2Z(35),NLZ
COMMON /BOU/ E1,E,BT(2)
DIMENSION R(1),WU(1),AZZ(35)
C
NLZ1=NLZ-1
DO 1 I=1,NLZ1
  AZZ(I)=0.5*(AZ(I)-AINF)
1 CONTINUE
AZZ(NLZ)=AZ(NLZ)-AINF
CALL F02BFF(AZZ,BZ,B2Z,NLZ,1,1,1,E1,E,E2,IZ,R,WU)
BT(1)=R(1)
CALL F02BFF(AZZ,BZ,B2Z,NLZ,NLZ,NLZ,1,E1,E,E2,IZ,R,WU)
BT(2)=R(1)
FN=BT(2)-ABS(BT(1))
RETURN
END

```

PROGRAM GAPTDTI

(single gap band)

```

PROGRAM GAPTDTI(SYM,TAPE4=SYM,INPUT,OUTPUT,TAPE5=INPUT,
+TAPE6=OUTPUT)

```

```

C
C   Program GAPTDTI attempts to calculate the terminating
C   parameters for an arbitrary set of coefficients describing
C   a band with a single gap. The procedure is an extension of
C   previous work on the connected band termination and uses
C   the terminator of Turchi, Ducastelle and Treglia to
C   construct a finite complex non-Hermitian tridiagonal matrix
C   at the band and gap edges. Some of the eigenvalues of this
C   matrix are related to the terminating coefficients A(i).
C   The User is required to supply the coefficients A(i),
C   B2(i) and the number of levels (pairs of coefficients) (s)he
C   wishes to be included in the calculation. In addition, the
C   User must provide the program with a guess as to the position
C   of the gap in the energy spectrum, in the form of the number
C   of energy eigenvalues in the lower and upper sub-bands. This
C   will allow the User to also supply an initial estimate of the
C   parameters a, W, g, G.

```

```

C
C
C   VARIABLES IN PROGRAM GAPTDTI

```

COMMON BLOCKS:

```

C   A(30),B2(30) = Continued fraction coefficients.
C   NL           = Number of levels in calculation (number
C                 of pairs of coefficients).
C   I1           = Number of energy eigenvalues in lower
C                 sub-band.
C   I2           = Number of energy eigenvalues in upper
C                 sub-band.
C   D1L,D1U      = Lower & upper values for D1 output by
C                 EDGEMAT.
C   D2           = W or G input to function EDGEMAT.
C   X2           = a or g input to function EDGEMAT.
C   IG           = Flag : = 0 working on full band:
C                   X1 = a , D1 = W ;
C                   X2 = g , D2 = G .
C                   = 0 working on gap:
C                   X1 = g , D1 = G ;
C                   X2 = a , D2 = W .
C   SEPS         = Error tolerance for self-consistency
C                 iteration.
C                 Applies only to W and G. Iteration
C                 proceeds until smallest error is
C                 within SEPS.
C   REPS         = Error tolerance for root finding
C                 routine. Input to library routine.
C   WCONV,GCCONV = "Convergences" of root finding routine

```

```

C                                     for W and G.  Given by 0.5*(D1U-D1L).
C
C
C
C
C      LOCAL:
C
C      NS          = Number of sets of coefficients in data file.
C      NC          = Number of pairs of coefficients in each set.
C      NEX         = Number of exact pairs.
C
C
C
C
C      WRITE HEADER
C
C      WRITE(6,9003)
9003  FORMAT(" CALCULATION OF TDT SINGLE BAND GAP TERMINATION",/,
+        " PARAMETERS USING FINITE COMPLEX NON-HERMITIAN",/,
+        " TRIDIAGONAL MATRIX AT GAP AND BAND EDGES.",//)
C
C      READ IN INTEGER DATA
C
C      READ(4,*) NS
C      READ(4,*) NC,NEX
C
C      LOOP OVER ALL SETS OF COEFFICIENTS
C
C      DO 1 I = 1,NS
C
C      READ COEFFICIENTS OF SET I
C
C      DO 2 J = 1,NC
C      READ(4,*) A(J),B2(J)
2      CONTINUE
C      WRITE(6,9000) I,NS
9000  FORMAT(" SET",I2," OF",I2, "READ",/)
C
C      ASK FOR USER-SUUPPLIED DATA
C
C      3  PRINT *,/,"INPUT NO. OF LEVELS AND NO.S OF EIGENVALUES",/,
+        "IN LOWER AND UPPER SUB-BANDS",
C
C      IF CARRIAGE RETURN ON EMPTY LINE, GO ON TO NEXT SET
C
C      READ(5,*,END=1) NL,I1,I2
C
C      CHECK CONSISTENCY OF EIGENVALUE COUNTING
C
C      IF ((I1+I2).GT.NL) THEN
C      WRITE(6,9004)
9004  FORMAT(" TOO MANY EIGENVALUES COUNTED INTO SUB-BANDS")
C      GOTO 3
C      ELSE
C      IF ((I1+I).LT.(NL-1)) THEN
C      WRITE(6,9005)

```

```

9005          FORMAT(" ONLY ONE EIGENVALUE ALLOWED IN GAP")
              GOTO 3
              ENDIF
              ENDIF
          4    PRINT *, "INPUT INITIAL ESTIMATES FOR AC,W,G,GC",
C
C IF CARRIAGE RETURN ON EMPTY LINE GO BACK TO REQUEST FOR NL,I1,I2
C
          READ(5,*,END=3) AC,W,G,GC
C
C CHECK CONSISTENCY OF INITIAL ESTIMATES
C
          IF ((G-GC).LT.(AC-W).
+           OR.
+           .(G+GC).GT.(AC+W)) THEN
              WRITE(6,9006)
9006          FORMAT(" DATA INCONSISTENT - GAP MUST BE WITHIN BAND")
              GOTO 4
          ENDIF
C
C DO ITERATION TO SELF-CONSISTENCY
C
          IFAIL=0
          CALL SELFIT(AC,W,G,GC,IFAIL)
          IF (IFAIL.NE.0) GOTO 3
C
C WRITE SELF-CONSISTENT VALUES FOR PARAMETERS
C
          WRITE(6,9001) AC,W,WCONV,G,GC,GCCONV
9001          FORMAT(/," SELF-CONSISTENT PARAMETERS :",/,
+           " AC =",F12.6,"    W  =",F12.6,"+/-",F7.6,/,
+           " G  =",F12.6,"    GC =",F12.6,"+/-",F7.6,/)
C
C ASK FOR ANOTHER NL,I1,I2
C
          GOTO 3
          1 CONTINUE
C
C CALCULATIONS COMPLETE
C
          WRITE(6,9002)
9002          FORMAT(////)
          STOP
          END
C
C
C
C
C

```

```

SUBROUTINE SELFIT(AC,W,G,GC,IFAIL)
COMMON /GAP/ D1L,D1U,D2,X2,IG
COMMON /ACC/ SEPS,REPS,WCONV,GCCONV
DIMENSION IQ(5)
EXTERNAL ABS

```

```

C
C
C

```

```

C   Subroutine SELFIT performs the iteration to self-
C consistency between the full band and the gap
C calculations necessary for the determination of the
C parameters a, W, g, G. It requires as input an estimate
C of the terminating parameters which is supplied by the
C User. The routine then iterates between calculation for
C the full band using ROOT and calculation for the gap
C using ROOT until, to some given accuracy, there is no
C further change in the parameters obtained.

```

```

C
C
C

```

```

C VARIABLES IN SUBROUTINE SELFIT

```

```

C
C
C

```

```

COMMON BLOCKS :

```

```

C
C
C

```

```

C   D1L,D1U      = Lower & upper values for D1 output by
C                 EDGEMAT.
C   D2           = W or G input to subroutine ROOT.
C   X2           = a or g input to subroutine ROOT.
C   IG           = Flag: = 0   working on full band
C                 = 1   working on gap.
C   SEPS         = Error tolerance for self-consistency
C                 iteration. Applies only to W and G.
C                 Iteration continues until the smallest
C                 error is within SEPS.
C   REPS         = Error tolerance for the root-finding
C                 routine. Input to library routine.
C   WCONV,GCCONV = "Convergence" of root-finding routine
C                 for W and G. Given by 0.5*(D1U-D1L).

```

```

C
C

```

```

PASSED IN/OUT :

```

```

C
C
C

```

```

C   AC,W,G,GC    = On Entry:  Estimates of the values of
C                         the parameters a, W, g, G.
C                         Supplied by the User.
C                 On Exit:   Self-consistent values for
C                         a, W, g, G.

```

```

C
C

```

```

C      LOCAL :
C
C      ACO,W0      = Values of parameters at previous step
C      GO,GCO      in iteration.
C      IQ          = Character array used to interrogate User.
C      ERR
C      IC
C      ICLIMIT
C
C
C
C
C      SET LIMITS TO NUMBER OF ITERATIONS
C
C      ICLIMIT=0
C      IC=0
C      3 ICLIMIT=ICLIMIT+5
C
C      BEGIN ITERATION
C
C      2 CONTINUE
C
C      SET OLD VALUES OF PARAMETERS
C
C      ACO=AC
C      W0=W
C      GO=G
C      GCO=GC
C      IC=IC+1
C
C      FIND ROOT FOR FULL BAND
C
C      IG=0
C      X2=GO
C      D2=GCO
C      CALL ROOT(AC,W,CONV,IFAIL)
C      IF (IFAIL.NE.0) GOTO 1
C      WCONV=CONV
C      ERR=AMAX1(ABS(AC-ACO),ABS(W-W0))
C
C      IF ERROR LESS THAN SEPS, RETURN TO MAIN PROGRAM
C
C      IF (ERR.LE.SEPS) RETURN
C
C      FIND ROOT FOR GAP
C
C      IG=1
C      X2=ACO
C      D2=W0
C      CALL ROOT(G,GC,CONV,IFAIL)
C      IF (IFAIL.NE.0) GOTO 1
C      GCCONV=CONV
C
C$$$
C$$$...INSERTED TO FOLLOW TRAJECTORY OF ITERATIONS
C$$$

```

```

      WRITE(6,8000) IC,AC,W,G,GC
8000  FORMAT(" ITERATION",I3," AC,W,G,GC =",4F10.6)
C$$
C$$
      ERR=AMAX1(ERR,ABS(G-GO),ABS(GC-GCO))
C
C IF MAXIMUM ERROR IS LESS THAN SEPS, ITERATION
C IS COMPLETE AND CONTROL RETURNS TO MAIN PROGRAM
C
      IF (ERR.LE.SEPS) RETURN
      IF (IC.LT.ICLIMIT) GOTO 2
      CONTINUE
C
C LIMITING NUMBER OF ITERATIONS PERFORMED.
C INTERROGATE USER ON EXTENSION
C
      WRITE(6,9000) ICLIMIT
9000  FORMAT(I4," ITERATIONS COMPLETED")
      PRINT *,"FURTHER ITERATIONS DESIRED",
      READ(5,9001,END=4) IQ
9001  FORMAT(5A1)
C
C IF MORE ITERATIONS DESIRED, ADD 5 TO LIMIT AND CONTINUE
C
      IF (IQ(1).EQ."Y") GOTO 3
C
C NO MORE ITERATIONS DESIRED. WRITE HEADER IN ANTICIPATION
C OF PRINTING OF PARAMETERS IN MAIN PROGRAM
C
      4 WRITE(6,9002)
9002  FORMAT(/," PRESENT VALUES OF")
      RETURN
C
C IF IFAIL NOT ZERO THEN ERROR IN ROOT
C
      1 CONTINUE
      IF (IFAIL.EQ.-1) THEN
C
C NO ROOT FOUND FOR X1; RETURN TO MAIN PROGRAM
C
      RETURN
      ELSE
C
C ERROR IN LIBRARY ROUTINES
C
      WRITE(6,9003)
9003  FORMAT(" ERROR IN C05",/)
      ENDIF
      STOP
      END
C
C
C

```

```

SUBROUTINE ROOT(X1,D1,CONV,IFAIL)
COMMON /GAP/ D1L,D1U,D2,X2,IG
COMMON /ACC/ SEPS,REPS,WCONV,GCCONV
EXTERNAL EDGEMAT
C
C
C   Given X2,D2 subroutine ROOT finds the values of X1,D1
C   at the point where function EDGEMAT = 0. It requires
C   an indication of the region of values of X1 within
C   which this root lies.
C
C
C   VARIABLES IN SUBROUTINE ROOT
C
C   COMMON BLOCKS :
C
C       D1L,D1U  = Lower & upper values for D1 output by EDGEMAT.
C       D2       = W or G input to subroutine ROOT.
C       X2       = a or g input to subroutine ROOT.
C       IG       = Flag : = 0 working on full band,
C                 = 1 working on gap.
C       SEPS     = Error tolerance in self-consistent iteration.
C       REPS     = Error tolerance in root finding routine. Input to
C                 library routine.
C       WCONV,   = "Convergence" of root finding routine for W and G.
C       GCCONV   Given by 0.5*(D1U-D1L).
C
C   PASSED IN/OUT :
C
C       X1       = ON ENTRY : Estimate of value of X1 at which
C                       EDGEMAT = 0.
C                       ON EXIT : Value of X1 where EDGEMAT = 0.
C       D1       = ON ENTRY : Estimate of value of D1 when
C                       EDGEMAT = 0.
C                       ON EXIT : Value of D1 when EDGEMAT = 0.
C       CONV     = ON EXIT : "Convergence" of root finding technique,
C                       = 0.5*(D1U-D1L).
C
C
C   SET ACCURACY OF LIBRARY ROUTINE
C
C       EPS=REPS
C
C   LOCATE REGION OF X1 IN WHICH ROOT LIES.
C   CHECK OUT TO +/- 0.5*MAX(D1,D2).
C
C       D1R=0.05*AMAX1(D1,D2)
C       IC=0
C       2 CONTINUE
C           IC=IC+1
C           X1L=X1-D1R*FLOAT(IC)
C           X1U=X1+D1R*FLOAT(IC)
C           DUM1=EDGEMAT(X1L)
C           DUM2=EDGEMAT(X1U)

```

```

C
C IF EDGEMAT OF OPPOSITE SIGN AT ENDS OF REGION THEN
C ROOT LIES WITHIN REGION
C
      IF (DUM1*DUM2.LT.0.0) GOTO 1
      IF (IC.LT.10) GOTO 2
      CONTINUE
C
C NO ROOT FOUND WITHIN +/- 0.5*MAX(D1,D2) OF X1
C
      WRITE(6,9000) X1L,X1U,X1,D1,X2,D2
9000 FORMAT(" ROOT OF EDEMAT NOT FOUND IN ",F7.3,"LT X1 LT",F7.3/,
+          " ESTIMATES OF PARAMETERS IN ROOT :",/,
+          " X1,D1,X2,D2 = ",4F7.3,/)
      IFAIL=-1
      RETURN
1 CONTINUE
C
C ROOT BETWEEN X1L AND X1U. USE LIBRARY ROUTINE TO FIND ROOT = X1
C TO ACCURACY EPS
C
      IFAIL=0
      CALL C05ABF(X1L,X1U,EPS,EDGEMAT,X1,IFAIL)
      IF (IFAIL.NE.0) GOTO 1000
C
C CALCULATE VALUES FOR D1 AND CONV AT THE ROOT
C
      DUM=EDGEMAT(X1)
      D1=0.5*(D1L+D1U)
      CONV=0.5*ABS(D1U-D1L)
C
C RETURN TO CALLING ROUTINE WITH X1,D1,CONV
C
1000 RETURN
      STOP
      END
C
C
C
      FUNCTION EDGEMAT(X1)
      COMMON /CFS/ A(30),B2(30),NL,I1,I2
      COMMON /GAP/ D1L,D1U,D2,X2,IG
      DIMENSION AR(30,30),AI(30,30),RR(30),RI(30),INT(30)
C
C
C The FUNCTION EDGEMAT takes as input the coefficients A(i), B2(i)
C and the band parameters X2,D2 (corresponding to a of g and W or G)
C and from these constructs the (possibly complex) finite
C tridiagonal matrix at the edges corresponding to X1 and D1.
C This edge matrix is diagonalised and the real parts of two of the
C eigenvalues, RR(i), picked out according to the input parameters
C I1, I2 and IG. The absolute magnitudes of these eigenvalues
C are returned as D1L and D1U, while EDGEMAT is returned as
C D1U-D1L.

```

```

C
C
C  VARIABLES IN FUNCTION EDGEMAT
C
C  COMMON BLOCKS :
C
C    A(30),B2(30) = Sets of continued fraction coefficients.
C    NL           = Number of pairs of coefficients in calculation.
C    I1           = Number of energy eigenvalues in lower sub-band.
C    I2           = Number of energy eigenvalues in upper sub-band.
C    D1L,D1U      = Lower & upper values for D1 output by EDGEMAT.
C    D2           = W or G input to function EDGEMAT.
C    X2           = a or g input to function EDGEMAT.
C    IG           = Flag : = 0 Working on full band
C                   X1 = a , D1 = W , X2 = g , D2 = G .
C                   = 1 Working on gap
C                   X1 = g , D1 = G , X2 = a , D2 = W .
C
C  PASSED IN/OUT :
C
C    X1           = g or a input to function at which eigenvalues
C                  will be calculated.
C
C  LOCAL :
C
C    AR(30,30)    = Real parts of edge matrix elements.
C    AI(30,30)    = Imaginary parts of edge matrix elements.
C    RR(30)       = Real parts of eigenvalues.
C    RI(30)       = Imaginary parts of eigenvalues.
C    INT(30)      = Workspace.
C    IA           = First dimension of AR,AI.
C
C
C    NL1=NL+1
C    NL2=NL+2
C    IA=30
C
C  CONVERT TO LOCAL VARIABLES
C
C    X1L=X1
C    X2L=X2
C    D2L=D2
C    IGL=IG
C
C  SET EDGE MATRIX = 0
C
C    DO 2 I=1,IA
C      DO 2 J=1,IA
C        AR(I,J)=0.0
C        AI(I,J)=0.0
C      2 CONTINUE
C
C  SET UP DIAGONAL AND PARA DIAGONAL ELEMENTS
C  TO (NL,NL) , (NL,NL+1) , (NL+1,NL)

```

```

C
C  NOTE ENTRY OF 2.0*SQRT(B2(NL+1))
C
      DO 3 I=1,NL
        AR(I,I)+A(I)-X1L
        AR(I,I+1)=SQRT(B2(I+1))
        AR(I+1,I)=AR(I,I+1)
      3 CONTINUE
      AR(NL,NL1)=2.0*SQRT(B2(NL1))
      AR(NL1,NL)=AR(NL,NL1)
C
C  CALCULATE ADDITIONAL TERMINATOR ELEMENTS
C
      ANL1=A(NL1)-2.0*X1L+X2L
      ANL2=X2L-A(NL1)
      B2NL2=ANL1*ANL2+D2L*D2L-4.0*B2(NL1)
C
C  ENTER DIAGONAL TERMINATOR ELEMENTS TO MATRIX
C
      AR(NL1,NL1)=ANL1
      AR(NL2,NL2)=ANL2
C
C  ENTER PARA DIAGONAL TERMINATOR ELEMENTS TO MATRIX
C
      IF (B2NL2.GE.0.0) THEN
C
C  B2NL2.GE.0.0 : MATRIX ELEMENTS (NL+1,NL+2), (NL+2,NL+1)
C                ARE REAL
C
        AR(NL1,NL2)=SQRT(B2NL2)
        AR(NL2,NL1)=AR(NL1,NL2)
      ELSE
C
C  B2NL2.LT.0.0 : MATRIX ELEMENTS (NL+1,NL+2), (NL+2,NL+1)
C                ARE IMAGINARY
C
        AI(NL1,NL2)=SQRT(-B2NL2)
        AI(NL2,NL1)=AI(NL1,NL2)
      ENDIF
C
C  DIAGONALISE MATRIX
C
      IFAIL=0
      CALL F02AJF(AR,IA,AI,IA,NL2,RR,RI,INT,IFAIL)
      IF (IFAIL) 1000,4,1000
      4 CONTINUE
C
C  PICK EIGENVALUES TO GIVE D1L,D1U and D1
C
      IF (IGL.EQ.0) THEN
C
C  FOR FULL BAND : EIGENVALUES ARE EXTREMAL
C

```

```

      RMIN=RR(1)
      RMAX=RR(1)
      DO 1 I=2,NL2
        RMIN=AMIN1(RMIN,RR(I))
        RMAX=AMAX1(RMAX,RR(I))
1     CONTINUE
      D1LL=ABS(RMIN)
      D1UL=RMAX
      ELSE
        IF (IGL.EQ.1) THEN
C
C   FOR GAP : EIGENVALUES GIVEN BY I1,I2
C             - I1 ENERGY EIGENVALUES IN LOWER SUB-BAND BRACKETED
C               BY EDGE MATRIX EIGENVALUES : I1+1 th
C             - I2 ENERGY EIGENVALUES IN UPPER SUB-BAND BRACKETED
C               BY EDGE MATRIX EIGENVALUES : NL+2-I2 th
C
C   SORT EIGENVALUES IN ASCENDING ORDER
C
      IFAIL=0
      CALL M01ANF(RR,1,NL2,IFAIL)
      IF (IFAIL.NE.0) GOTO 1000
C
C   PICK OUT EIGENVALUES OF INTEREST
C
      D1LL=ABS(RR(I1+1))
      D1UL=RR(NL2-I2)
      ELSE
        WRITE(6,9000) IGL
        STOP
      ENDIF
    ENDIF
C
C   RETURN WITH D1L,D1U FOR GIVEN X1
C   (GIVEN X2,D2 ETC.)
C
      D1L=D1LL
      D1U=D1UL
      EDGEMAT=D1UL-D1LL
      RETURN
9000 FORMAT(" IGL =",I3," THEREFORE STOP")
1000 STOP
      END

```