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TIGHT-BINDING USING THE RECURSION METHOD *

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ABSTRACT

The recursion method is reviewed and a new terminator for the continued fraction representation of the Green function is presented. A comparison with other known terminators is made by reconstructing known functions. Test calculations of the density of states in bcc-Fe is done using the first principles canonical tight-binding description of O.K. Andersen for the construction of the Hamiltonian in a cluster of 400 atoms. The calculation required a small amount of CPU-time and it was performed on a personal computer. Compared with more exact k-space methods, the result reveals that the essential features of the DOS are very well reproduced, even the saturation magnetization.

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1. Introduction

Normally the calculation of the density of states (DOS) in disordered systems prevents the use of k-space techniques because of the lack of Bloch's theorem, and real space methods have to be used.

The use of supercell calculations, in which one recovers the periodicity of the system by imposing periodic boundary conditions, is dangerous when certain "peaks" in the DOS appear due to the periodicity and in practice, various sizes of the supercell have to be calculated in order to discover which features in the DOS are caused by the boundary conditions. This is particularly difficult in systems having delocalized electrons.

The DOS, $D(E)$, is related to the the number of states (NOS), $N(E)$, up to certain energy E ,

$$N(E) = \int_{-\infty}^E dx D(x) \quad (1)$$

Moreover, if we know the spectra of eigenvalues $\{E_l\}$, then

$$N(E) = \sum_{\text{levels}} g_l \Theta(E - E_l) \quad (2)$$

where the factor g_l is the degeneracy of the level l , and $\Theta(x)$ is the Heaviside step function (i.e. $\Theta(x) = 1$ if $x \geq 0$ and $\Theta(x) = 0$ if $x < 0$).

From Equations (1) and (2) we have

$$D(E) = \frac{dN(E)}{dE} \quad (3)$$

and

$$D(E) = \sum_{\text{levels}} g_l \delta(E - E_l) = \sum_{\text{states}} \delta(E - E_s) \quad (4)$$

In the last summation we suppress the factor g_l because we sum over states. Normally we formulate the physical problem by modelling the Hamiltonian, \hat{H} in some basis of functions reasonably complete and orthogonal. Then Eq.(4) can be written as:

$$D(E) = \text{Tr} \delta(E - \hat{H}). \quad (5)$$

This is of course a rather formal definition of $D(E)$ because the spectrum of \hat{H} is unknown, and it is what we want to calculate.

However this definition is useful for the relation between the DOS and the Green operator defined as:

$$\hat{G}(z) = (z - \hat{H})^{-1} \quad (6)$$

which can be calculated for each z by knowing the Hamiltonian in some representation.

The inverse of the operator $(z - \hat{H})^{-1}$ can be found by taking the trace of \hat{G}

$$\text{Tr} \hat{G}(z) = \sum_s \langle s | \hat{G} | s \rangle = \sum_s G_{ss}(z), \quad (7)$$

which is an invariant. In the representation in which \hat{H} is diagonal we have:

$$\text{Tr} \hat{G}(z) = \sum_s \frac{1}{z - E_s}, \quad (8)$$

and, using Eq(4) this relation can be written as:

$$\text{Tr} \hat{G}(z) = \int_{-\infty}^{\infty} dx \frac{D(x)}{z - x}. \quad (9)$$

The inversion of this relation for a given energy E is achieved by taking the imaginary part of $\hat{G}(z)$ in $z = E - i\zeta$:

$$\frac{1}{\pi} \text{Im Tr} \hat{G}(E - i\zeta) = \frac{1}{\pi} \sum_s \frac{\zeta^2}{(E - E_s)^2 + \zeta^2}, \quad (10)$$

in the limit $\zeta \rightarrow 0^+$ the Lorentz curve of Eq.(10) becomes a Dirac delta function (in the sense of a distribution), so that we finally get the relation

$$\lim_{\zeta \rightarrow 0^+} \frac{1}{\pi} \text{Im Tr} \hat{G}(E - i\zeta) = \sum_s \delta(E - E_s) = D(E). \quad (11)$$

If we want to calculate only the partial density of states associated with some "orbital" α of the basis functions, in which we have our Hamiltonian matrix we do not need to calculate the trace of $\hat{G}(z)$ but just the leading element $G_{\alpha\alpha}$ in the same representation as the Hamiltonian.

The local DOS associated with the orbital α , $D_\alpha(E)$ is given by:

$$D_\alpha(E) = \lim_{\zeta \rightarrow 0^+} \frac{1}{\pi} \text{Im} G_{\alpha\alpha}(E - i\zeta). \quad (12)$$

The Green function is related with the moments of the partial DOS μ_n defined as:

$$\begin{aligned} \mu_n &= \int_{-\infty}^{\infty} d\epsilon D_\alpha(\epsilon) \epsilon^n = \langle \alpha | \hat{H}^n | \alpha \rangle \\ &= \sum_{\beta \gamma \delta \dots \epsilon} \langle \alpha | \hat{H} | \beta \rangle \langle \beta | \hat{H} | \gamma \rangle \dots \langle \epsilon | \hat{H} | \alpha \rangle, \end{aligned} \quad (13)$$

which is related with closed paths counting in a lattice defined by the set of orbitals $\{\alpha\}$, beginning from the α orbital hopping around its neighbouring orbitals and returning to α . Normally \hat{H} is given in a tight binding representation so that the elements $\langle \alpha | \hat{H} | \beta \rangle$ in Eq.(13) only connect orbitals α, β if they are neighbours.

The local DOS can be reconstructed from its moments by using a continued fraction expansion of the integral giving the diagonal element of the Green function¹:

$$G_{\alpha\alpha}(z) = \int_{-\infty}^{\infty} dx \frac{D_\alpha(x)}{z - x} \quad (14)$$

$$= \frac{\alpha_1}{z + \alpha_2 - \frac{\alpha_2 \alpha_3}{z + \alpha_3 - \alpha_4 - \frac{\alpha_4 \alpha_5}{z + \alpha_5 - \alpha_6 - \dots}}}$$

where the coefficients α_i are given by:

($n > 0$, $\mu_0 = 1 = \alpha_1$, i.e. the DOS is normalized)

$$\alpha_{2n} = \frac{\Delta_{n-2} \Delta'_{n-1}}{\Delta_{n-1} \Delta'_{n-2}}, \quad (15)$$

$$\alpha_{2n+1} = \frac{\Delta_n \Delta'_{n-2}}{\Delta_{n-1} \Delta'_{n-1}},$$

where the Δ 's are the following determinants: ($\Delta_{-1} = \Delta'_{-1} = 1$):

$$\Delta_n = \det \begin{vmatrix} \mu_0 & \cdot & \cdot & \mu_n \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \mu_n & \cdot & \cdot & \mu_{2n} \end{vmatrix}, \quad (16)$$

$$\Delta'_n = \det \begin{pmatrix} \mu_1 & \cdot & \cdot & \mu_{n+1} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \mu_{n+1} & \cdot & \cdot & \mu_{2n+1} \end{pmatrix}$$

This method is known² to be very unstable because the evaluation of the Δ determinants with increasing order moments is very difficult. An easy way to understand this point is to analyze a DOS which is normalized and non-zero in the $(=,1)$ interval (by rescaling the energy) then it is easy to see that

$$0 \leq \mu_n \leq M \frac{1}{n+1}, \quad (17)$$

where M is the maximum of $D(E)$ in the $(0,1)$ interval and therefore $\mu_n \rightarrow 0$ as $n \rightarrow \infty$, hence Δ_n , and $\Delta'_n \rightarrow 0$ for large values of n .

Another way to obtain a continued fraction representation of the elements of the Green function is given by the recursion method.

2. Recursion Method

The origin of the Recursion method is due to Lanczos³ and essentially is a method for transforming a symmetric matrix into a tridiagonal form. The modern version of the recursion method connecting it with solid state physics problems was given by R. Haydock⁴. The recursion method is a real space method for the calculation of the Green function elements and local DOS. In order to calculate the local DOS associated with some electron orbital α ,

$$D_\alpha(E) = \frac{1}{\pi} \text{Im} G_{\alpha\alpha}(E - i0^+), \quad (18)$$

we begin by 'placing' the electron some particular orbital α , defining an initial state for the system (the initial vector for the tridiagonalization process) which is:

$$|1\rangle = (0, 0, \dots, 1, 0, 0, \dots)^\dagger \quad (19)$$

By defining a recurrence relation we generate a new basis $\{|n\rangle\}$. In this new basis the original Hamiltonian \hat{H} has a tridiagonal form.

$$\hat{H} = \begin{pmatrix} a_1 & b_1 & & & \\ b_1 & a_2 & b_2 & & \\ & b_2 & a_3 & b_3 & \\ & & & \cdot & \cdot \\ & & & & \cdot \end{pmatrix} \quad (20)$$

The recurrence relations which define the transformation to the tridiagonal form are ($n = 2, 3, \dots$)

$$b_1 |2\rangle = \hat{H} |1\rangle - a_1 |1\rangle, \quad (21)$$

$$b_n |n+1\rangle = \hat{H} |n\rangle - a_n |n\rangle - b_{n-1} |n-1\rangle$$

The a_n, b_{n-1} are the coefficients to orthogonalize $\hat{H} |n\rangle$ to the preceding vectors, $|n\rangle$ and $|n-1\rangle$, and b_n is the coefficient to normalize $|n+1\rangle$ to unity.

The coefficients $\{a_n, b_n\}$ are given by:

$$a_n = \langle n | \hat{H} | n \rangle \quad (22)$$

$$b_n = \langle n+1 | \hat{H} | n \rangle$$

They describe, as we will see, higher order moments of the density of states and represent the influence of atoms increasingly remote from the chosen orbital α on the local DOS.

The new vectors generated by the Lanczos recursion method defined in Eq.(21) generate an orthonormal set in the Krylov subspace¹ $\{|1\rangle, \hat{H} |1\rangle, \hat{H}^2 |1\rangle, \dots, \hat{H}^{n-1} |1\rangle\}$.

The basic Lanczos procedure can be viewed as a Gram-Schmidt orthogonalization of the set of Krylov vectors $\{|1\rangle, \hat{H} |1\rangle, \hat{H}^2 |1\rangle, \dots\}$

The new basis is therefore generated by repeated operation with \hat{H} , each operation allowing the electron to hop further from the initial orbital α . This procedure is very easy to implement numerically, because we need to perform only matrix multiplications. However, round off errors due to finite precision

¹Given a $n \times n$ H matrix and a starting vector $|v\rangle$, the family of Krylov subspaces K^κ , $\kappa = 1, 2, \dots, n$ is defined as follows:
 $K^\kappa = \text{space}\{|v\rangle, H |v\rangle, H^2 |v\rangle, \dots, H^{\kappa-1} |v\rangle\}$

computers, make possible that the new vectors generated after some iterations are not orthogonal to all the preceding ones.

In practice to improve the numerical stability of the recursion the formulae given in Eq.(22) are replaced by the following ones:

$$\begin{aligned} a_n &= \langle n | (\hat{H} | n \rangle - b_n | n-1 \rangle) \quad , \quad (23) \\ b_n &= \langle \hat{H} | n \rangle - a_n \langle n | n-1 \rangle \end{aligned}$$

From Eq.(19) it is easy to calculate $G_{\alpha\alpha}(E) = \langle \alpha | (E - \hat{H})^{-1} | \alpha \rangle = \langle 1 | (E - \hat{H})^{-1} | 1 \rangle$, because $E - \hat{H}$ is:

$$E - \hat{H} = \begin{pmatrix} E - a_1 & -b_1 & 0 & 0 & \dots \\ -b_1 & E - a_2 & -b_2 & 0 & \dots \\ 0 & -b_2 & E - a_3 & 0 & \dots \\ \cdot & \cdot & \cdot & \cdot & \dots \end{pmatrix} \quad (24)$$

We denote by D_0 the determinant of Eq.(24), by D_1 the determinant of Eq.(24) when the first row and column are omitted, by D_2 the determinant when the first and second rows and columns are omitted, etc., then $\langle 1 | (E - \hat{H})^{-1} | 1 \rangle$, the leading element of the inverse of this matrix, is:

$$G_{\alpha\alpha} = \frac{\det D_1}{\det D_0} = \frac{1}{\det D_0 / \det D_1} \quad (25)$$

Now, $\det D_0 = (E - a_1) \det D_1 - b_1^2 \det D_2$, hence

$$G_{\alpha\alpha} = \frac{1}{(E - a_1 - \frac{b_1^2}{\det D_1 / \det D_2})} \quad (26)$$

Similarly:

$$\frac{\det D_1}{\det D_2} = E - a_2 - \frac{b_2^2}{\det D_2 / \det D_3}, \quad (27)$$

etc.. This yield the continued fraction representation of $G_{\alpha\alpha}$:

$$G_{\alpha\alpha}(E) = \frac{1}{E - a_1 - \frac{b_1^2}{E - a_2 - \frac{b_2^2}{E - a_3 - \frac{b_3^2}{\dots}}}} \quad (28)$$

The comparison of this expression with Eq.(14) gives the explicit relation between the moments of the local DOS and the recursion coefficients.

Due to the finite size of the Hamiltonian matrix, which implies that we are studying a finite cluster, and due to computer time reasons, one is limited to calculate up to some level in the recursion coefficients. For electronic structure calculations of bulk properties in transition metals we usually stop after the 10-th level for the recursion coefficients of the s and p partial DOS, and after the 20-th level for the d-states.

The reason for this is that the electronic s- and p-states are of long range order compared with the d-states, so that going beyond the 10-th level in the calculation of the partial DOS for the most central atoms in clusters of around 1500 atoms introduces non negligible surface effects, which modifies the shape of the partial DOS.

However, for an accurate recovery of the singularities of the DOS, such as band edges and van Hove singularities within the bands, it would be necessary to consider too many recurrences. This is done in practice by truncating the continued fraction with a terminator $T(z)$ after some level n.

$$G_{\alpha\alpha}(z) = \frac{1}{z - a_1 - \frac{b_1^2}{z - a_2 - \frac{b_2^2}{z - a_3 - \dots - a_n - b_n^2 T(z)}}} \quad (29)$$

Here $T(z)$ is a terminator applied at the n-th level. Its introduction does not alter the first 2n-moments of the partial DOS.

3. Terminator

Normally one uses the 'square root terminator' after the last calculated level. This terminator assumes that after the n-th level the coefficients are taken as constants and equal to their asymptotic limits a_∞, b_∞ . These values are directly related to the band limits E_B, E_T (bottom and top of the band)²:

$$\begin{aligned} a_\infty &= \frac{1}{2} (E_T + E_B) \quad , \quad (30) \\ b_\infty &= \frac{1}{2} (E_T - E_B) \quad . \end{aligned}$$

However, the asymptotic limits are generally not known and the square root terminator gives often spurious oscillations in the DOS curve, specially when a gap is present, due to the abrupt matching between the known calculated coefficients and the asymptotic ones.

The most common implementation of this terminator which evaluates the asymptotic values a_∞ and b_∞ with the calculated coefficients is due to Beer and Pettifor⁵.

More sophisticated approaches for terminating the continued fraction have been given by C.Nex^{6,7}.

We now introduce a different type of terminator. To this effect we note that the recursion method, which transforms the Hamiltonian \hat{H} to a tridiagonal form, is equivalent to transform the original problem into a semi-infinite linear chain and then asking for the Green function matrix element on the surface atom:

$$\hat{H} \Rightarrow \sum_{n=1} |n\rangle a_n \langle n| + \sum_{n=1} (|n\rangle b_n \langle n+1| + |n\rangle b_{n-1} \langle n-1|) \quad (31)$$

$(b_0 = 0)$

$$\begin{array}{ccccccccc} a_1 & & b_1 & & a_2 & & b_2 & & a_3 & & b_3 & & a_4 & & b_4 & & a_5 & \dots \\ \hline 1 & & & & 2 & & & & 3 & & & & 4 & & & & 5 & \dots \end{array}$$

The physical interpretation of a terminator T which is applied after the n -level of recursion is to introduce some effective medium around the atom in which we are interested. Then we expect this medium to be less important if the terminator is applied as far as possible from the surface atom, and with a smooth matching with the calculated coefficients.

The procedure we used for terminating the continued fraction given in Eq.(29) is based on the existence of band limits and asymptotic values for the recursion coefficients, which satisfy the relation of Eq.(30).

For the following analysis it is convenient to rewrite the continued fraction given in Eq.(29) by the following relation:

$$x_n = E - a_n - \frac{b_n^2}{x_{n+1}}, \quad (32)$$

$n = 1, 2, \dots$

The assumption of the asymptotic values implies that

$$x_\infty = E - a_\infty - \frac{b_\infty^2}{x_\infty}, \quad (33)$$

By solving this equation for x_∞ one finds⁸

$$x_\infty = b_\infty e^{i\phi}, \quad (34)$$

where $\phi = \cos^{-1} \left(\frac{E - a_\infty}{2b_\infty} \right)$, $-\pi < \phi < \pi$

We examine the expression given in Eq.(32) in the asymptotic region by defining

$$\begin{aligned} x'_n &= x_n - x_\infty, \\ a'_n &= a_n - a_\infty, \\ b'_n &= b_n - b_\infty. \end{aligned} \quad (35)$$

Eq.(32) can now be written as follows:

$$x'_n + x_\infty = (E - a_\infty) - a'_n - \frac{(b_n'^2 + 2b'_n b_\infty + b_\infty^2)}{(x'_{n+1} + x_\infty)} \quad (36)$$

By keeping only linear terms in b'_n and using Eq.(34) we get the following recurrence relation for x'_n :

$$x'_n = -a'_n - 2b'_n e^{-i\phi} + e^{-2i\phi} x'_{n+1} \quad (37)$$

Now, defining $-a'_n$ and $-2b'_n$ as the even and odd terms of a single sequence δ_n ,

$$\begin{aligned} \delta_{2n} &= -a'_n, \\ \delta_{2n+1} &= -2b'_n, \end{aligned} \quad (38)$$

we obtain

$$x'_n = \delta_{2n} + \delta_{2n+1} e^{-i\phi} + x'_{n+1} e^{-2i\phi}, \quad (39)$$

hence by iterating:

$$x'_n = \delta_{2n} + \delta_{2n+1} e^{-i\phi} + \delta_{2n+2} e^{-2i\phi} + \delta_{2n+3} e^{-3i\phi} + \dots$$

We know that in the limit $x'_n \rightarrow 0$, so that x'_n has a form of a Fourier series:

$$x'_n = \sum_{k=0}^{\infty} \delta_{2n+k} e^{-ik\phi} \quad (40)$$

$$-\pi < \phi < \pi.$$

The coefficients are given by:

$$\delta_m = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\phi x'_n(\phi) e^{i(m-2n)\phi}. \quad (41)$$

From this expression we know the δ sequence up to a certain level from the calculated coefficients. The idea was to extrapolate the δ sequence by using all first known values of δ_n .

The fitting was done simply by a least square procedure. This is equivalent to assume that after some level M all terms of the sequence δ_k are a linear combination of all the preceding ones:

$$\delta_k = \sum_{j=1}^M c_j \delta_{k-j} \quad k > M. \quad (42)$$

In terms of the new vectors which are generated by the recursion procedure the last relation indicates that for studying those states the first M vectors alone generate all the space. The relation given in Eq.(42) is equivalent to assuming that the δ sequence can be written as follows:

$$\delta_n = \sum_{i=1}^M d_i z_i^n, \quad (43)$$

where z_i are the roots of the following polynomial:

$$z^M - \sum_{j=1}^M c_j z^{M-j} = 0. \quad (44)$$

Eq.(43) is the same as the assumption made by Allan⁹ to find the best fit of the δ 's.

If one uses Eq.(42) separately for the a_n and b_n sequences the problem is then reduced to the one studied by Trias et al¹⁰.

4. Test Calculations

In order to check the quality of the linear terminator we applied it to reconstruct known functions for which we can calculate the moments of the DOS. Using Eqs.(14)-(16) we find the coefficients $\{a_n, b_n\}$ appearing in Eq.(28)

$$a_n = \frac{1}{\Delta'_{n-2}} \left(\frac{\Delta_{n-2} \Delta'_{n-1}}{\Delta_{n-1}} + \frac{\Delta_{n-1} \Delta'_{n-3}}{\Delta_{n-2}} \right), \quad (45)$$

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

The test functions we used (all normalized) are given by:

$$D(x) = \begin{cases} 1 & 0 < x < 1 \\ 0 & \text{elsewhere} \end{cases};$$

$$D(x) = \begin{cases} \frac{1}{2} \sqrt{x} & 0 < x < 1 \\ 0 & \text{elsewhere} \end{cases}; \quad (46)$$

$$D(x) = \begin{cases} 1 - \cos(4\pi x) & 0 < x < 1 \\ 0 & \text{elsewhere} \end{cases};$$

$$D(x) = \begin{cases} 1 & 0 < x < \frac{1}{2} \\ 2 & \frac{3}{4} < x < 1 \\ 0 & \text{elsewhere} \end{cases}.$$

The present calculations were done on a personal computer with single precision. For all the above functions we calculated the Δ determinants and through Eq.(45) the coefficients a_n, b_n up to $n = 7$. The results of applying the terminator $T(z)$ of the Cambridge Recursion Library of Nex⁷, the one of Beer and Pettifor⁵ and the linear terminator after the $n=7$ level in the continued fraction of Eq.(29) and then using Eq.(18) for recover the initial function $D(x)$ are shown in Figs.(1-4).

The linear terminator was used by extrapolating up to 500 pairs of coefficients and then using the asymptotic limits (i.e., a_{500} and b_{500}) for closing the continued fraction with the square root.

The main result obtained by using the linear terminator is the suppression of spurious peaks in the DOS in all functions $D(x)$ which do not have a gap. In

the $D(x)$ function which has a gap the linear method produces also spurious peaks which arise principally because the condition given in Eq.(30) is not satisfied in the case of gaps. In these cases the asymptotic values of a_n and b_n show undamped oscillations^{2,11}.

Terminators which can be applied for studying DOS containing a gap (i.e. for semiconductors) have been studied in Refs.11-12.

5. Application to bcc-Fe

As a concrete physical application for studying the electronic structure of metals we wanted to test the method with bcc-Fe, and with amorphous $Fe_{80}B_{20}$ systems¹³.

For the construction of the Hamiltonian we used the first principles formulation of a tight binding Hamiltonian based on the Linear Muffin Tin Orbital Method of Andersen et al^{14,15}.

The calculation of the local DOS at a Fe-atom in bcc-Fe was done using a finite cluster. The Fe-cluster was built using 400-atoms which were fully coordinated up to the second nearest neighbour shell (in total this makes around 1500 atoms).

The positions of the atoms correspond to those of an ideal Fe bcc-crystal, with the experimental lattice parameter of $a = 2.681 \text{ \AA}$ (i.e., a Wigner Seitz radius of 2.662 a.u.). For the construction of the Hamiltonian \hat{H} , we have used the non screened potential parameters¹⁵ corresponding to the Fe-bcc periodic structure with the same lattice parameter (C, E_p, Δ and Q). We have transformed these non screened potential parameters to the screened ones (tight-binding \tilde{C} and $\tilde{\Delta}$) using the following relations¹⁵:

$$\tilde{C} = C - (Q - \tilde{Q}) \frac{(C - E_p)^2}{\Delta}, \quad (47)$$

$$\tilde{\Delta}^{\frac{1}{2}} = \frac{(\tilde{C} - E_p)}{(C - E_p)} \Delta^{\frac{1}{2}}.$$

with $\tilde{Q}_s = 0.03485$, $\tilde{Q}_p = 0.05303$ and $\tilde{Q}_d = 0.010714$. The tight binding Hamiltonian H is built according to:

$$H = \tilde{C} + \tilde{\Delta}^{\frac{1}{2}} \tilde{S} \tilde{\Delta}^{\frac{1}{2}}. \quad (48)$$

Here \tilde{S} is the screened structure constant matrix¹⁵, (a matrix of range 400x9), and was built by inverting 400 times smaller matrices of range 15x9, and keeping each time the first line. 15 is the total number of atoms in a small cluster with bcc structure including first and second nearest neighbours, and 9 is the number of orbitals (s-, p- and d-states) per atom considered.

The calculation of the partial DOS was done on the most central Fe-atom in the cluster, using the recursion method described in the preceding sections with the linear terminator extrapolating up to the level 500.

The results for the calculated recursion coefficients using Eqs.(21) and (23) (a_n, b_n) up to $n=30$ for the p-electronic states are shown in Fig.(5).

One sees that after the 14th level the coefficients corresponding to the p_x, p_y and p_z states are different. This fact is due to the lack of cubic symmetry around the central Fe atom in the cluster of 400 particles. This is also reflected for the two kinds of d-states (those with E_g and T_{2g} symmetry) but in this case the surface effects are not so strong before the 17th level, this is because the d-states are more localized than the p- and s-states. For the evaluation of the DOS 7, 9 and 17 pairs of calculated recursion coefficient for the s-, p- and d-states respectively were used for the extrapolation procedure. The results for the partial s, p and d DOS curves are shown in Fig.(6) together with the results obtained for the infinite periodic case using more exact k-space techniques and the same approximation for the Hamiltonian and the lattice parameter¹⁵.

The calculation of the partial NOS gives the following occupation for the s, p and d states ($s=0.83$, $p=0.85$, $d=6.32$ total 8 electrons) and the Fermi energy at $E_F = -0.111$ Ry. The corresponding values for the 'exact' calculation of paramagnetic bcc-Fe, where the f-electronic states were also considered are: $E_F = -0.125$ Ry, $s=0.633$, $p=0.751$, $d=6.528$ and $f=0.088$.

6. Discussion

Considering that the local DOS at the Fe atom in the bcc cluster was performed using a personal computer, and a finite number of recursion coefficients, the agreement between the 'exact' and approximated DOS curves is excellent.

From the result shown in Fig.(4) it seems that the linear terminator does not

work when a gap is present. However if the gap is sufficiently small compared with the total band width, the oscillations of the recursion coefficients are still sinusoidal and a perturbation theory is still valid^{11,16}. However, in order to take into account the oscillations of the coefficients in an efficient way more than 7 pairs of coefficients are needed in our example. More sophisticated terminator have been recently developed by R. Haydock and C.Nex¹².

Despite the shortcoming of the linear terminator when there is a gap, it provides the best way to obtain accurately the band limits and the suppression of spurious oscillations in the DOS curves allow not only to study integrated quantities also but local quantities.

For testing this last point we also performed a more detailed study of the density of states around the Fermi level by calculating the magnetization of the Fe atom. We used the Stoner model with k-independent exchange splitting¹⁷. In this model the selfconsistent condition for a ferromagnetic state is that the integral of the paramagnetic DOS per spin, over an energy range ΔE around the Fermi energy equals the magnetization m . In this model:

$$\Delta E = mI,$$

where I is the Stoner parameter for Fe ($I \approx 70 \text{ mRy}^{15}$).

In terms of the function $\bar{N}(m)$ which is the average DOS per spin around the Fermi level over a range of m spins selfconsistency requires that.

$$\frac{m}{\Delta E} = \bar{N}(m).$$

Then by plotting $\bar{N}(m)$ as a function of m (the number of unpaired electrons) we see that the Stoner criterium is satisfied when:

$$\bar{N}(m) = \frac{1}{I}.$$

Fig.(7) shows this plot and one can see that the magnetization is $1.99\mu_B$ or $2.10\mu_B$ depending on which density of states we use for the evaluation of \bar{N} . Strictly this Stoner model is valid for localized d-electrons¹⁷, but the influence of the s-states is negligible as one can see from the Fig.(6). This is because the s-partial DOS is very small around the Fermi level.

The experimental value for the saturation magnetization of bcc Fe is $2.2\mu_B$

and a full selfconsistent LMTO tight binding calculation including spin polarization gives the value¹⁶ $m=2.18\mu_B$.

This result shows that the recursion method allows to studying magnetic properties. A calculation of the same type for Fe in a cluster with a fcc structure reveals no magnetic moment (i.e. the $\bar{N}(m)$ curve lies below I^{-1} for all values of m), so that fcc Fe is a paramagnetic system.

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Figure Captions

Figure 1. Reconstruction of the first function of Eq.(46) using the the first 7 pairs $\{a_n, b_n\}$ of recursion coefficients and 3 terminators, Nex⁷, Beer-Pettifor⁵ and the one of the present work.

Figure 2. Same as figure 1, but with the second function of Eq.(46).

Figure 3. Same as figure 1, but with the third function of Eq.(46).

Figure 4. Same as figure 1, but with the fourth function of Eq.(46).

Figure 5. The a_n and b_n calculated recursion coefficients for the three p-states (p_x -, p_y - and p_z -symmetry) of the central Fe-atom in the 400-atom cluster.

Figure 6. The local DOS (s, p, d and total DOS) on the most central Fe-atom in the 400-atom cluster with bcc structure, the right pannel shows the results of a LMTO tight binding calculation for the infinite Fe bcc lattice¹⁵.

Figure 7. Stoner plot showing the $\bar{N}(m)$ and $1/I$ functions as a function of m ($I = 70\text{mRy}$). The intersection of the $\bar{N}(m)$ function with $1/I$ gives the value of the magnetization m . The upper curve is $\bar{N}(m)$ calculated with the total DOS, whereas for the lower curve only the d-partial DOS was used.

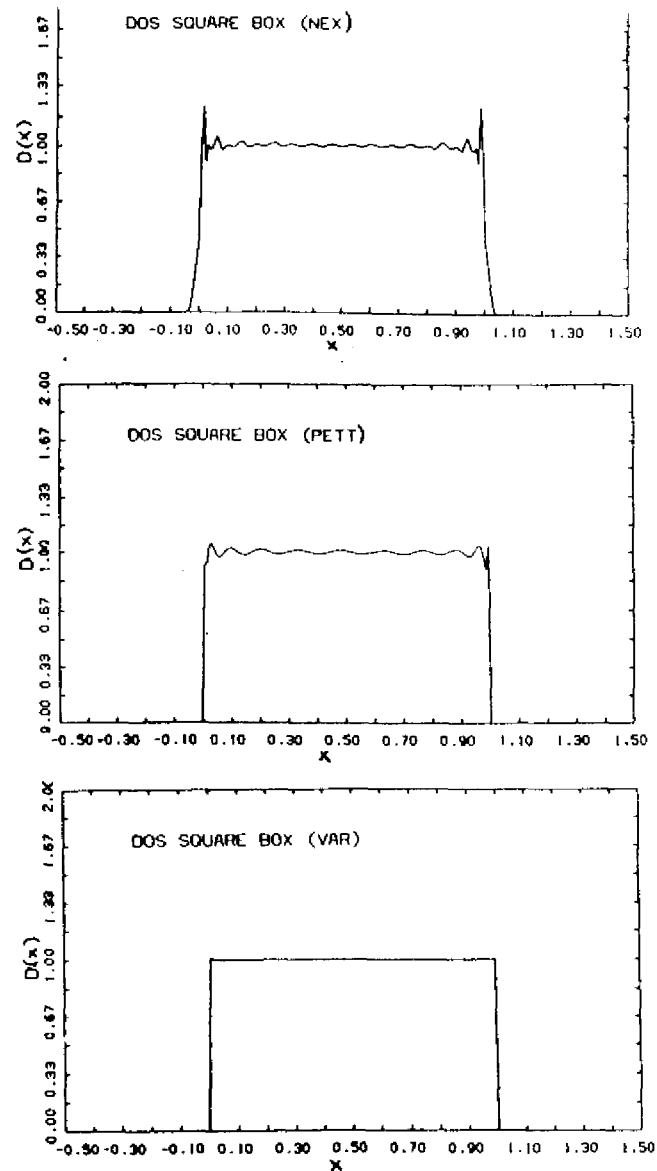


Fig.1

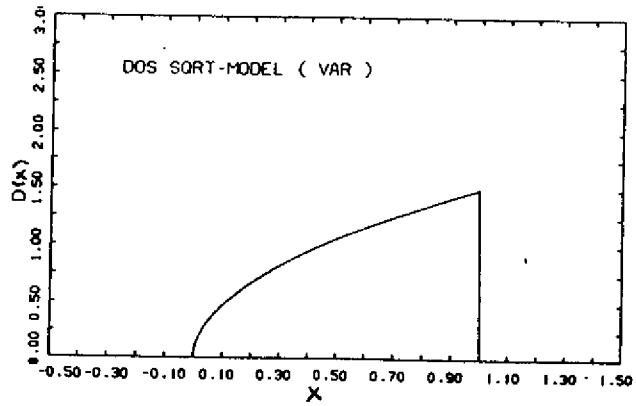
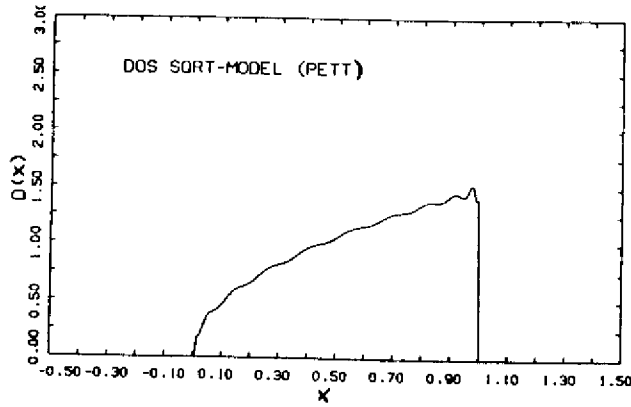
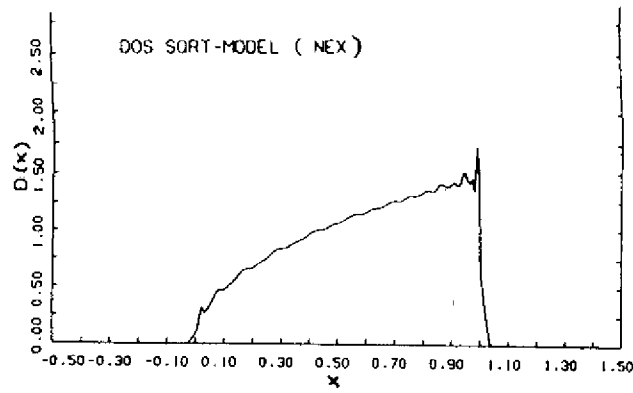


Fig.2

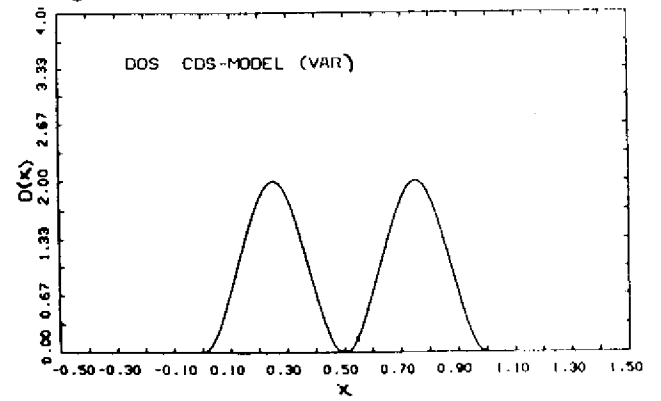
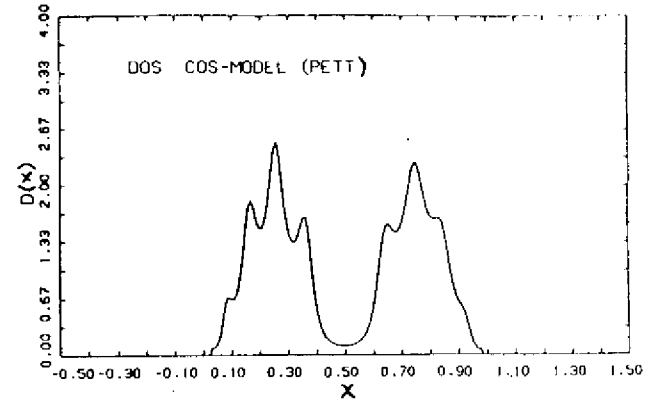
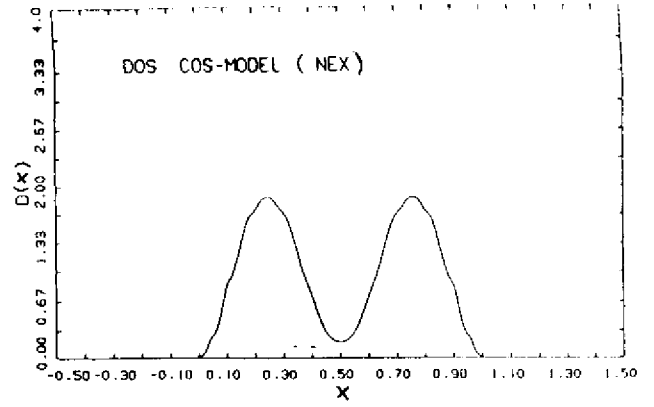


Fig.3

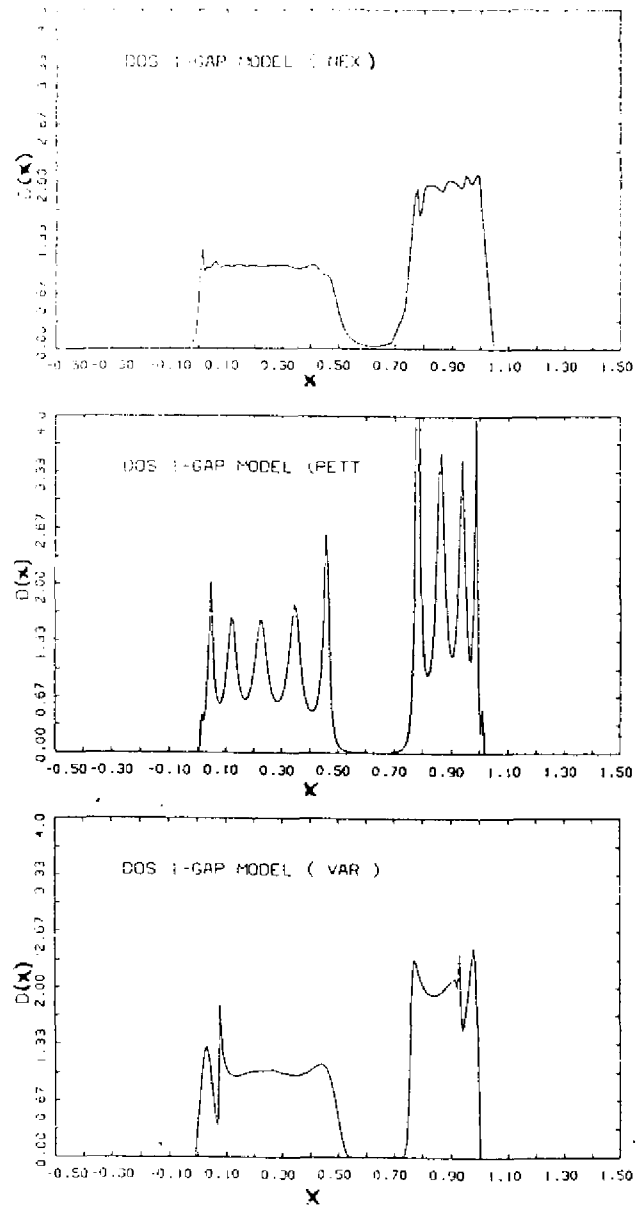


Fig.4

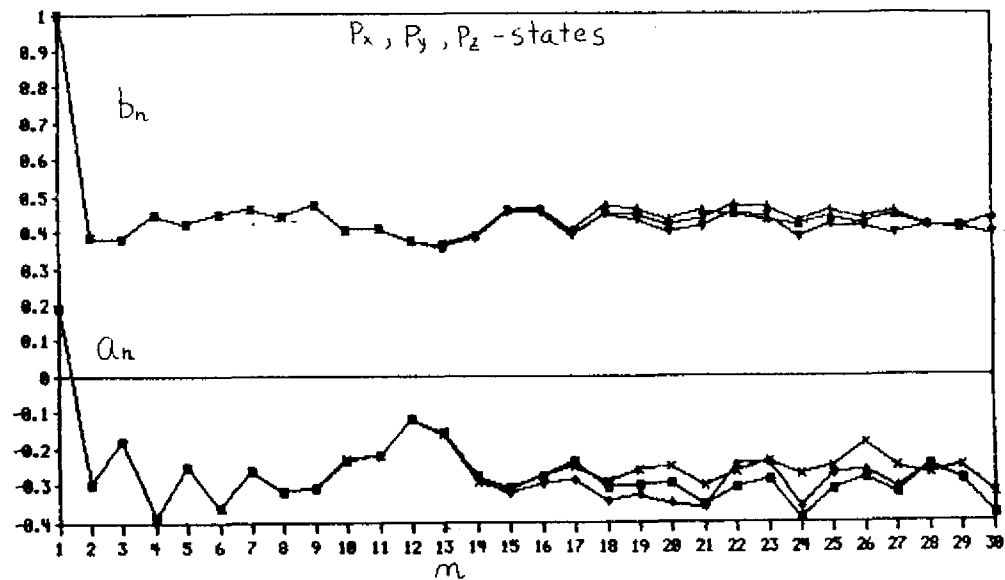


Fig.5

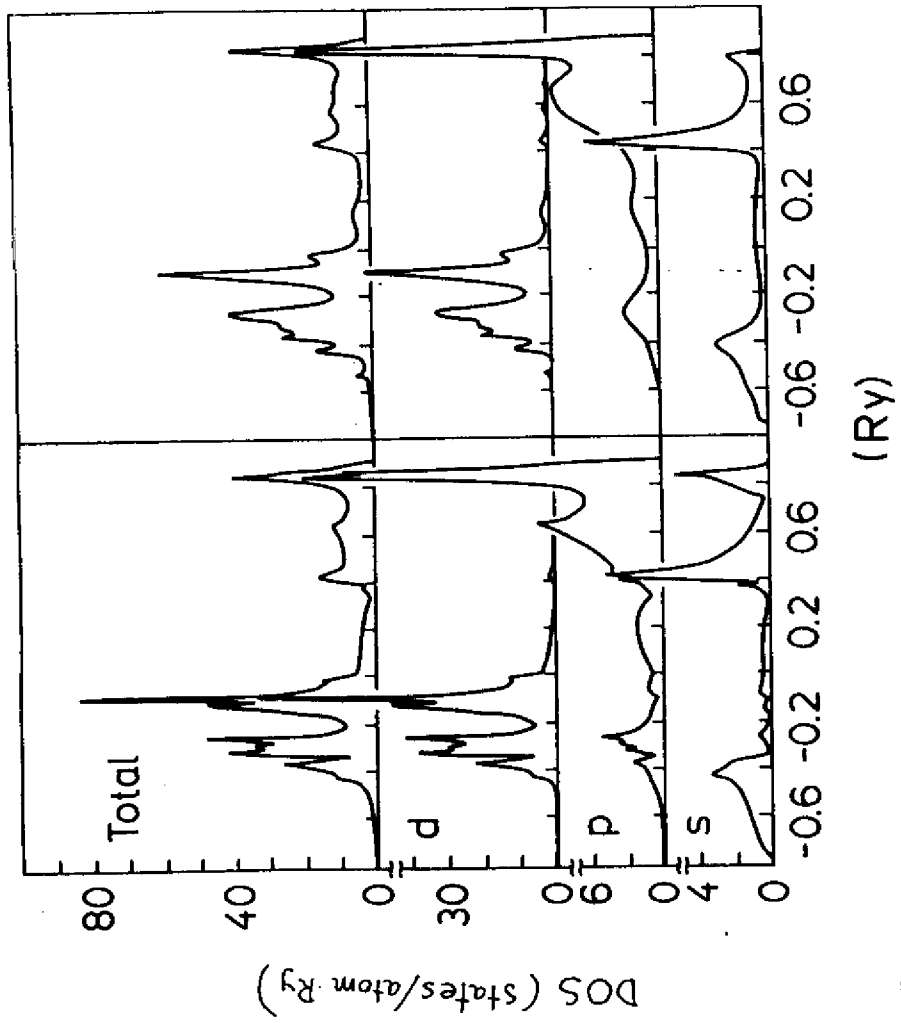


Fig.6

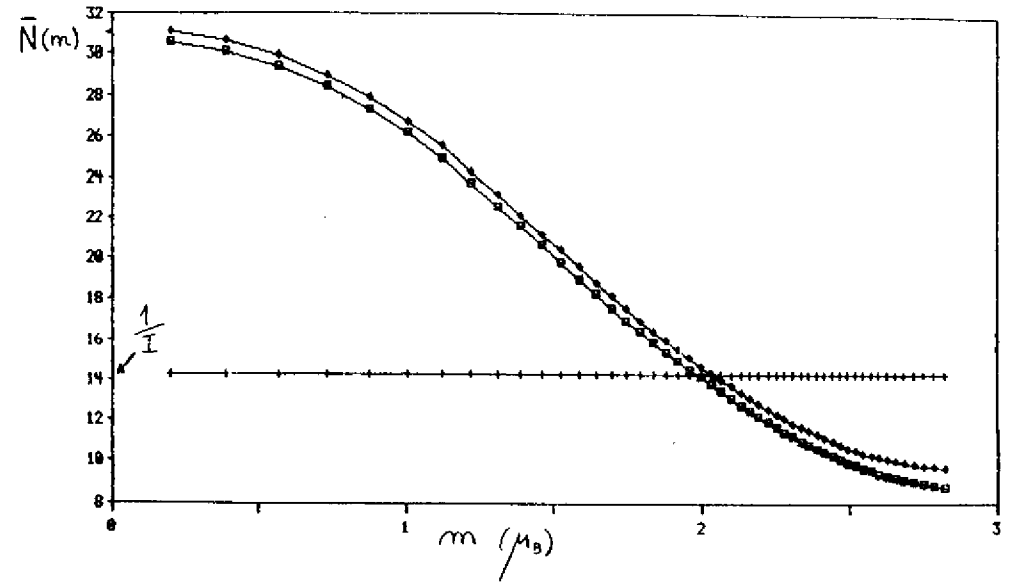


Fig.7

