A study of the convergence of the recursion method for metals and compounds

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Abstract

In a recent communication (Chakrabarti A and Mookerjee A 2001 *J. Phys.: Condens. Matter* **13** 10 149) we have introduced the generalization of the augmented space recursion (ASR) (Saha T, Dasgupta I and Mookerjee A 1994 *J. Phys.: Condens. Matter* **6** L245) technique for systems with many atoms per unit cell. In this paper we have justified the convergence properties of ASR by studying the convergence of various moments of local density of states and other physical quantities like Fermi energy and band energy of some ordered systems like V, Cu, Ni and Cu_3Au. We have also looked at the convergence of the magnetic moment of Ni, which is very sensitive to numerical approximations. Finally we have tried to establish that the recursion method is equally applicable for studying properties of ordered systems.

1. Introduction

The recursion method was introduced by Haydock *et al* [7, 8] as an elegant alternative to the then widely prevalent reciprocal space band structure techniques. The method was based on a completely real space formalism. It did not invoke any lattice translation symmetry and its consequent Bloch theorem. It was proposed as an ideal tool for studying the electronic properties of systems with broken symmetry [1]: surfaces and systems with substitutional and topological disorder. Although the recursion method was introduced almost thirty years ago, there still remains a residual scepticism about the accuracy and practical applicability, certainly for ordered systems.

In this paper we shall first carry out recursion calculations based on the tight-binding linearized muffin-tin orbitals (TB-LMTO) [2–4] method for various ordered metals and compounds. Then, in order to establish the fact that the recursion method is equally acceptable for predicting properties of the ordered systems studied, we shall compare our results with standard reciprocal space methods based also on the same TB-LMTO technique. Finally we shall carry out a thorough analysis of the convergence and accuracy of the technique. The aim

will be to handle convincingly the possible errors in the method, with a view of minimizing them within our tolerance limits.

2. The recursion method within a TB-LMTO basis

The recursion method provides an elegant and computationally efficient formalism for calculating the local electronic structure properties of elements and compounds. It is a real space technique, by which elements of the Green function associated with a sparse representation of a Hamiltonian are obtained by transforming the representation to a tridiagonal form. This is done by constructing a new orthonormal basis set $|n\}$ from the older one $|n\rangle$ by the following three term recursion formula:

$$|n + 1\} = H|n\} + \alpha_n|n\} + \beta_{n-1}^2|n - 1\}$$ (1)

with the initial choice $|1\} = |RL\alpha\rangle$, and $\beta_0^2 = 1$. These terms are explained in connection with the TB model described below.

The choice is guided by the fact that we are interested in obtaining $G_{RL\alpha,RL\alpha}(E)$. The coefficients α_n and β_n are obtained by imposing the ortho-normalizability condition of the new basis set. They are given by:

$$\frac{\{n|H|n\}}{\{n|n\}} = \alpha_n \qquad \frac{\{n|H|n-1\}}{\{n|n\}} = \beta_{n-1}^2 = \{n-1|H|n\} \qquad \{n|H|m\} = 0.$$ (2)

Now the diagonal elements of the Green function can be calculated from the following expression:

$$G_{RL\alpha,RL\alpha}(z) = \cfrac{1}{z - \alpha_1 - \cfrac{\beta_1^2}{z-\alpha_2-\cfrac{\beta_2^2}{z-\alpha_3-\ddots}}}.$$ (3)

The local density of states (LDOS) is related with the Green function by the following relation:

$$n(E) = -\frac{1}{\pi} \operatorname{Im} m\, G(E - i\delta^+).$$ (4)

In practice, the infinite continued fraction expression is evaluated to a finite number of steps. Haydock [6] has shown that the contributions from the continued fraction coefficients α_n and β_n can be mapped onto self-avoiding walks on the underlying lattice. He has shown that the dominant contributions come from those paths which wind around the initial starting state. This allows one to work on a subspace of the total Hilbert space in which the Hamiltonian is defined i.e., a finite sized cluster about the starting state.

As has been mentioned earlier, since the recursion method needs a localized basis for its operation, one can perform recursion in the framework of the TB-LMTO formalism. We now describe very briefly the methodology of recursion in the framework of the TB-LMTO.

The second order TB-LMTO Hamiltonian is written in terms of potential parameters and the screened structure matrix. It is given by

$$\mathcal{H}^{(2)} = E_v + h - hoh$$ (5)

where,

$$h = \sum_{RL\alpha}(\tilde{C}_{RL\alpha} - \tilde{E}_{RL\alpha})\mathcal{P}_{RL\alpha} + \sum_{RL\alpha}\sum_{R'L'\alpha'} \tilde{\Delta}_{RL\alpha}^{1/2}\, S_{RL\alpha,R'L'\alpha'}\, \tilde{\Delta}_{R'L'\alpha'}^{1/2}\mathcal{T}_{RL\alpha,R'L'\alpha'}$$ (6)

- C, o and Δ are potential parameters of the TB-LMTO method, these are diagonal matrices in the angular momentum indices. Also o^{-1} has the dimension of energy and is a measure of the energy window around $\tilde{E}$ within which the approximate Hamiltonian $\mathcal{H}^2$ is reliable.
- R denotes a *cell position* label associated with a TB-LMTO basis and $L = (\ell m m_s)$ is the composite angular momentum index. α denotes an atom in the Rth cell whose position is $R + \xi^\alpha$.
- $S_{RL\alpha, R'L'\alpha'}$ is called structure matrix, which depends only on the geometry of the underlying lattice.
- $\mathcal{P}_{RL\alpha}$ and $\mathcal{T}_{RL\alpha, R'L'\alpha'}$ are the projection and transfer operators in Hilbert space H spanned by tight-binding basis $\{|RL\alpha\rangle\}$: $\mathcal{P}_{RL\alpha} = |RL\alpha\rangle\langle LR\alpha|$ and $\mathcal{T}_{RL\alpha, R'L'\alpha'} = |RL\alpha\rangle\langle R'L'\alpha'|$.

Using the definition of Green function we can write

$$G_{RL\alpha, RL\alpha}(E) = \langle R, L, \alpha | (E\hat{I} - \hat{\mathcal{H}}^{(2)})^{-1} | R, L, \alpha \rangle.$$

3. Errors in the recursion method

We shall now study the various approximations necessary for practical applications of the recursion method and the consequent errors. We shall illustrate the nature of convergence of various calculated physical quantities which are basic for any electronic structure calculation. This study of convergence is essential because otherwise we will not be able to set the cut-offs of various parameters like number of shells in real space, recursion levels and so on, for numerical calculations and ensure that our numerical results are within our tolerance window.

Before we set out to analyse the errors in the method, let us first compare the results for the density of states for Cu, Cu_3Au, V and Ni as obtained from a forty-step recursion carried out on an exact twenty shell real-space map. The choice of the systems is deliberate. Cu is a full d-shell noble metal, V is a half-filled metal in the lower end of the transition series while Ni is a magnetic transition metal. Cu_3Au is an ordered alloy which is stable in the L12 arrangement on a fcc lattice, figures 1 and 2 show this comparison.

For Cu and Cu_3Au most of the detailed features of the density of states calculated from the recursion calculations match with the k-space results. As expected, the k-space results show sharper structures. The Fermi energies in both cases match to within a few hundredths of a rydberg. Both the majority and minority band density of states for ferromagnetic Ni are reproduced excellently in the recursion calculations. The agreement is equally good for V up to the Fermi energy. The unoccupied part of the band shows disagreement. However, it must be understood that the recursion is done with the second order Hamiltonian in the most localized representation of the TB-LMTO, while the k-space calculations are done with the orthogonal representation. A higher order recursion calculation should improve the unoccupied part of the band considerably.

How good are our results? When we talk of convergence of the recursion method, we have to be careful in stating precisely what we mean. Finite space approximants to Green functions do not converge for real energy values. This problem arises in every computational method, as noted by [9]. The problem definitely arises in the usual k-space integration techniques, where methods using either complex energies or complex k-s have been attempted. The cause of this non-convergence is that an arbitrary small perturbation, like adding a single atom to a large but finite system, can shift all eigenvalues of the system. This causes an infinite change in the Green function near its corresponding poles. Thus, the precise meaning of the convergence of the recursion should imply rather the convergence of physical quantities built out of it. Most physical quantities are averages over the spectrum of the type:
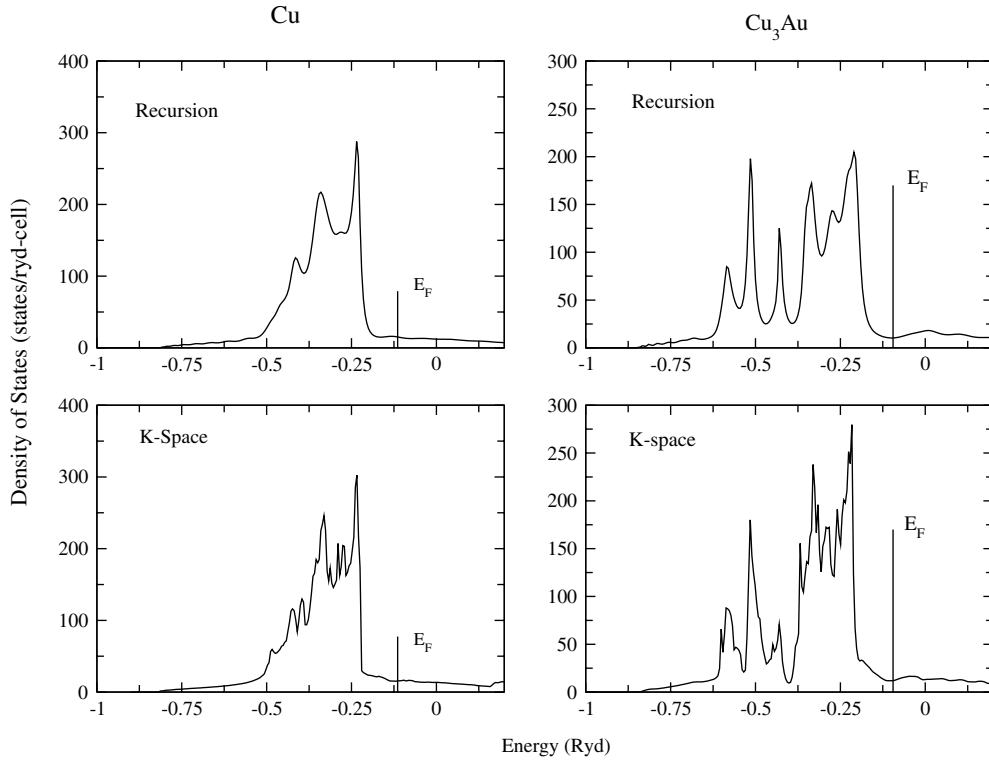
$$F(E) = \int_{E_0}^{E_F} f(E')\, n(E')\, dE'$$

Cu

Cu₃Au

Figure 1. The density of states for Cu and Cu₃Au using (top) the recursion method and (bottom) the k-space method.

E_0 is the lower band edge, and $f(E)$ is any smooth, well behaved function of E. It is the convergence of these quantities which will decide whether the recursion is convergent or not. For example, the Fermi energy is defined by

$$\int_{-E_0}^{E_F} n(E')\,\mathrm{d}E' \ = \ n_e$$

where n_e is the total number of electrons. While the band energy is

$$U \ = \ \int_{-E_0}^{E_F} E'\,n(E')\,\mathrm{d}E'.$$

We shall study, in general, the convergence of indefinite integrals of the kind

$$M_k(E) \ = \ \int_{-\infty}^{E} (E')^k\,n(E')\,\mathrm{d}E'.$$

The integrand E'^k is monotonic and well behaved within the integration range. A measure of the root-mean-square error in the moments is

$$\Delta_k \ = \ \left\{ \frac{1}{E_U - E_0}\left(\int_{E_0}^{E_U} (\delta M_k(E))^2\,\mathrm{d}E \ - \ \left(\int_{E_0}^{E_U} \delta M_k(E)\,\mathrm{d}E \right)^2 \right) \right\}^{1/2}. \quad (7)$$

Errors can arise in the recursion procedure because of two distinct sources: (i) the error that arises because we carry out a finite number of recursion steps and then terminate the continued
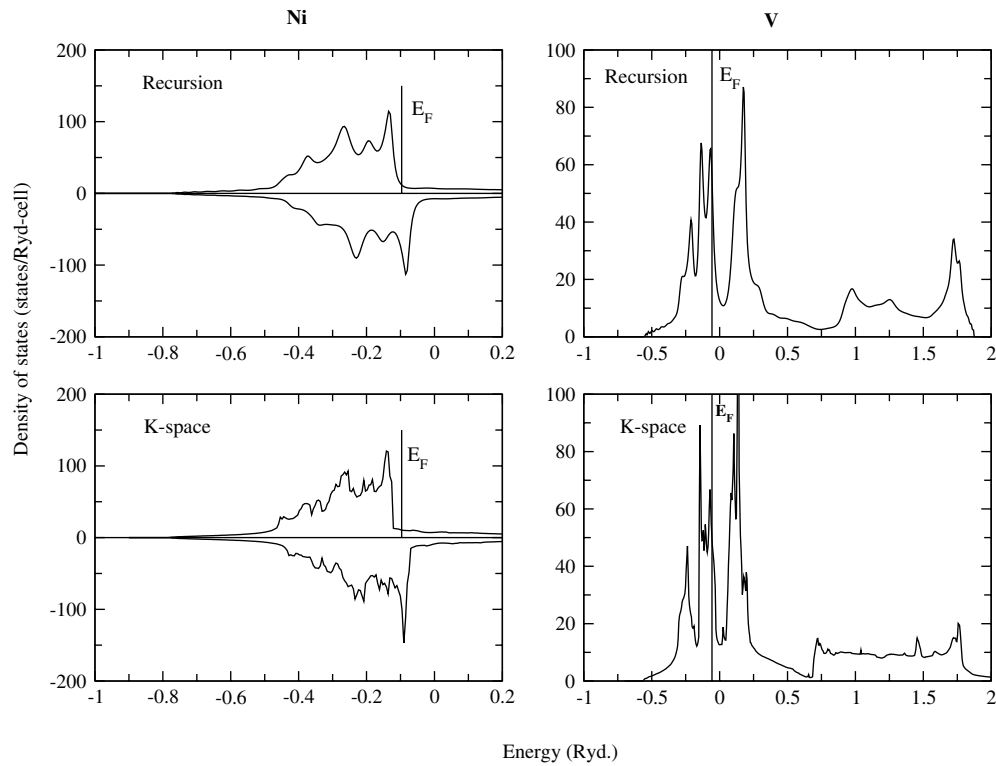
Figure 2. The density of states for Ni and V using (top) the recursion method and (bottom) the *k*-space method.

fraction using one of the available terminators (ii) the error that arises because we choose a large but finite part of the nearest-neighbour map and ignore the part of the augmented space very *far* from the starting state. Haydock has justified both these approximations by stating that (i) if the terminator is chosen so as to reflect the asymptotic behaviour of the continued fraction, errors should be small, and (ii) since we can write expressions for the continued fraction in terms of self-avoiding *walks* on the underlying lattice, long walks are dominated by those that wind round the starting state and do not go far away from it.

We shall first carry out a simple error analysis of the continued fraction expression for the Green function because of errors created on the continued fraction coefficients.

The recursion is a two-term recurrence relation. We may therefore generate from this a pair of linearly independent set of polynomials through the relations:

$$b_{n+1} X_{n+1}(E) = (E - a_n) X_n(E) - b_n X_{n-1}$$

where, $X_n(E)$ is either $P_n(E)$ or $Q_n(E)$ according to the initial conditions:

$$P_1(E) = 1 \qquad P_2(E) = (E - a_1)/b_2$$
$$Q_1(E) = 0 \qquad Q_2(E) = 1.$$

The approximated Green function in terms of the terminator $T(E)$ is given by:

$$G(E) = \frac{Q_{N+1}(E) - b_N Q_N(E) T(E)}{b_1 [P_{N+1}(E) - b_N P_N T(E)]}.$$

The terminator determines entirely the essential singularities of the the spectrum. Reference [9] showed that a finite composition of fractional linear transformations like the one above can at most add a finite number of poles to the spectrum. The essential singularities of the exact $G(E)$ and $T(E)$ coincide. The fractional linear transformation redistributes the spectral weights over the spectrum.

Let us now assume that we make errors $\{\delta a_n, \delta b_n\}$ in the corresponding continued fraction coefficients. If we now start generating the orthogonal polynomials, starting from the exact initial conditions, but with the errors in the continued fraction coefficients, we shall obtain a pair of sets $\{\tilde{P}_n\}$ and $\{\tilde{Q}_n\}$. In general we shall have,

$$\tilde{P}_n(E) = (1 + A_n(E))P_n(E) + B_n(E)Q_n(E).$$

If we substitute this back into the recurrence relation and keep only the first order terms in the errors,

$$A_n(E) = \{\delta a_n[P_{n+1}(E)Q_{n+1}(E)] + \delta b_n[P_n(E)Q_{n+1}(E) + P_{n+1}(E)Q_n(E)]\}/b_1$$
$$B_n(E) = \{-\delta a_n P_{n+1}(E)^2 - \delta b_n[2\,P_n(E)P_{n+1}(E)]\}/b_1.$$

Using the above and the expression for the LDOS, we find that the first order relative error produced in the LDOS

$$\frac{\delta n(E)}{n(E)} = -2\left[\left\{\sum_{n=1}^{\infty} A_n(E)\right\} + b_1 R(E)\left\{\sum_{n=0}^{\infty} B_n(E)\right\}\right]$$

where $R(E) = \mathcal{R}e\,G(E)$. If we define the weighted Hilbert transforms of $P_n(E)$ as the so-called associated functions:

$$Q_n(E) = \mathcal{R}e\left\{\int_{-\infty}^{\infty} \frac{P_n(E')n(E')}{E - E'}\,\mathrm{d}E'\right\}.$$

These associated functions are also solutions of the three-term recursion. They are not polynomials, but are nevertheless orthogonal to the set $P_n(E)$.

In terms of these, the error in the density of states is:

$$\frac{\delta n(E)}{n(E)} = \frac{2}{b_1}\left\{\sum_{n=1}^{\infty}[\delta a_n P_{n+1}(E)Q_{n+1}(E) + 2\,\delta b_{n+1} P_{n+1}Q_{n+2}]\right\}. \tag{8}$$

If the first N continued fraction coefficients are exact, that is in case we carry out our recursion on a N-shell neighbour map up to N steps and then terminate, the error in the various moment functions are:

$$\delta M_k(E) = +\sum_{n=N}^{\infty}\{\delta a_n A_n^{(k)}(E) + \delta b_{n+1} B_n^{(k)}(E)\} \tag{9}$$

where,

$$A_n^{(k)}(E) = \frac{2}{b_1}\int_{-\infty}^{E} P_{n+1}(E')Q_{n+1}(E')(E')^k n(E')\,\mathrm{d}E'$$

$$B_n^{(k)}(E) = \frac{4}{b_1}\int_{-\infty}^{E} P_{n+1}(E')Q_{n+1}(E')(E')^k n(E')\,\mathrm{d}E'.$$

From this expression and equation (6) we can obtain an expression for the overall error in the moments. Numerical results for the errors in the moment functions are shown in figure 3. The convergence in Fermi and band energies with number of recursion steps are shown in figures 4 and 5.

These are calculated on a 20 shell neighbour map and up to 40 steps in recursion. The figures clearly illustrate the convergence of the procedure with increasing recursion steps, as
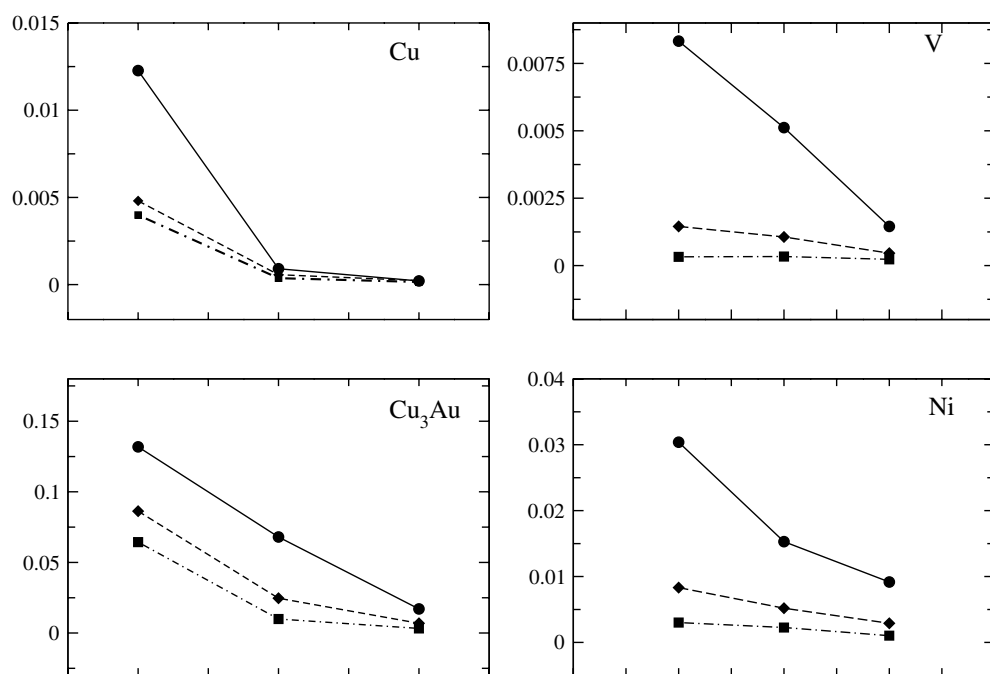
Figure 3. The root mean square errors in the first (full lines), second (dashed lines) and third (dashed dotted lines) moments of the density of states as functions of the recursion steps.
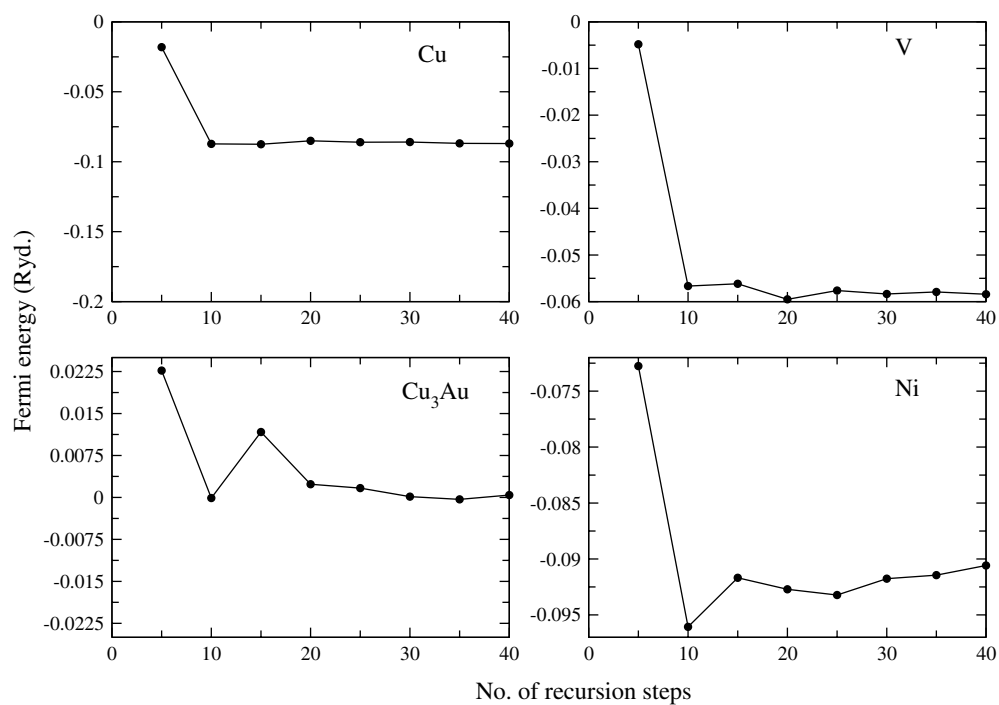

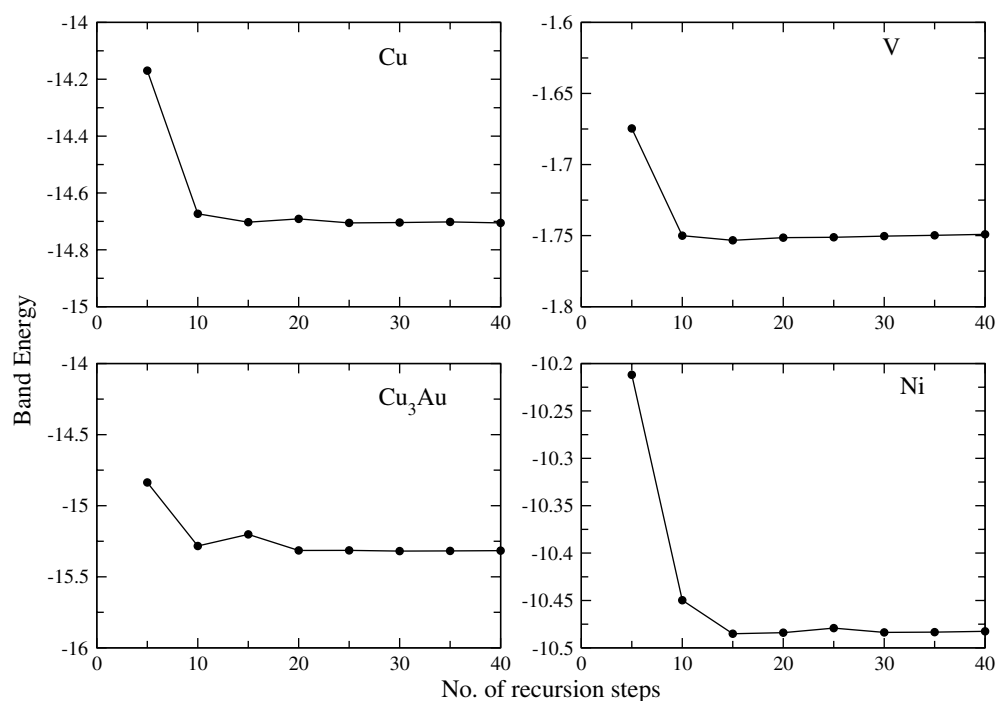**Figure 4.** The convergence with recursion step of the Fermi energies of Cu, Cu$_3$Au, Ni and V.

Figure 5. The convergence with recursion step of the band energies of Cu, Cu_3Au, Ni and V.
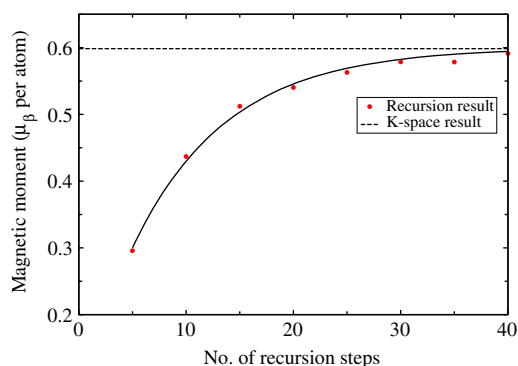

Figure 6. The convergence with recursion step of the magnetic moment of Ni.

surmised by Haydock. As expected the higher moments converge more rapidly. The rapid convergence of higher moments is at the basis of the reproduction of most of the density of states shape in an approximate recursion procedure. It should be noted, however, that as we carry out recursion beyond 40 steps, very soon the procedure becomes unstable. This instability arises due to two sources: (i) we have carried out recursion on a 20 shell neighbour-map. As we go beyond 20 steps of recursions, finite size effects begin to show up. Numerically till 40 steps these errors are tolerable. Beyond 45 they lead to instability. We can control this by increasing the size of the neighbour-map. (ii) Numerical cumulative errors lead to the loss of orthogonality in the recursion generated basis. This can be controlled by deliberately orthogonalizing after every 20 steps or so. In the presence of disorder, the sharp structures in

the density of states are smoothed by finite life-time effects. The convergence of the higher moments is even more rapid. The above analysis in ordered systems is therefore in a *worst scenario* situation.

Figure 7 shows the convergence of the magnetic moment of Ni as a function of the number of recursion steps towards the value 0.6 μB obtained from k-space techniques. Magnetic moment is a physical quantity which is very sensitive to the errors in numerical approximations. The figure shows that within 35–40 recursion steps on a 20 shell real-space map, the magnetic moment has converged within our error tolerance.

It is evident from the above analysis that the size of the neighbour map and the number of recursion steps required can vary from system to system. For every situation, we have to carry out this error analysis before we can rely on our numerical results with a degree of satisfaction.

4. Remarks and conclusion

In this paper we have compared the results obtained from the recursion method with that obtained from the reciprocal space method and argued that the former is also an accurate technique to calculate electronic structure calculation.

Finally we have analysed the convergence of the recursion technique in the worst case scenario of no disorder and have argued that disorder smooths out structure in the density of states, so that for disordered alloys the convergence of the moments is even faster.

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