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1994 J. Phys.: Condens. Matter 6 L245

(http://iopscience.iop.org/0953-8984/6/17/003)

J. Phys.: Condens. Matter 6 (1994) L245–L251. Printed in the UK

LETTER TO THE EDITOR

An augmented-space recursive technique for the calculation of electronic structure of random binary alloys

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Received 19 January 1994

Abstract. We present here a computationally feasible and fast technique for obtaining the electronic structure of random alloys which allows us to incorporate effects like clustering, short-range order and off-diagonal disorder arising out of size mismatch and consequent lattice distortions. The method combines the augmented-space technique with the recursion method and the tight-binding LMTO. AgPd alloys are studied to illustrate our procedure.

The linearized tight-binding muffin-tin orbital (TB-LMTO) method, introduced by Andersen and Jepsen [1], has been widely used to calculate the *ab initio* electronic structure of periodic solids. Recently the method has been successfully employed to study structures without perfect translational symmetry, such as substitutionally disordered alloys, surfaces, interfaces and others. Until recently, almost all of the work on substitutionally disordered alloys has been based on mean field approaches, the most successful amongst these being the coherent potential approximation (CPA). Recently Kudrnovský and Drchal [2] have demonstrated that the TB-LMTO-CPA can, in a large class of alloy systems, accurately describe the electronic structure of random alloys, both metallic and semiconducting, and disordered surfaces. The self-consistency involved in the solution of the CPA equation is not trivial and one has to invoke subtle mathematical procedures to ensure proper convergence. Moreover since the CPA is a single-site approximation, it has been pointed out time and again that it cannot take into account the problems like lattice relaxation and local stresses involving angular distortions and also short-range order. These lead to off-diagonal disorder in the Hamiltonian which cannot be treated in either an additive or multiplicative form, which reduces it to an equivalent diagonal disorder problem. Recently Singh and Gonis [3] have criticized the TB-LMTO-CPA proposed by Kudrnovský and Drchal on the grounds that ensemble or configuration averaging involved in their method did not properly take into account the multi-site nature of the TB-LMTO basis functions resulting in an inconsistency in the ensemble-averaged Green function. Although these authors try to circumvent this difficulty by making a pure-L approximation for the site diagonal linearized muffin-tin orbitals (LMTOs), the fact remains that, by its very nature, the TB-LMTO formalism involves multisite summations.

There have been attempts at self-consistent cluster generalizations of the CPA [4] to include clusters and short-range order, but their applications to date have been restricted to model systems.

An alternative and general approach to configuration averaging was proposed earlier [5]. This augmented-space formalism (ASF), although acknowledged as a powerful technique,

0953-8984/94/170245+07$19.50

has not found application except in simple, model systems. The main difficulty in its implementation is the enormous rank of the configuration space† and how to handle calculations on it. The purpose of this communication is to propose and implement a new method which is based on the ASF coupled with the recursion method of Haydock *et al* [6]. We shall handle the recursion on the full augmented space by reducing the Hamiltonian using the point group symmetries of the underlying real lattice and the larger symmetries in the configuration part of the augmented space arising out of the homogeniety of disorder. It was shown earlier by Gallagher [10] that if we start recursion with a state belonging to an irreducible subspace of a Hilbert space, subsequent recursion always stays within this subspace. This allows us significant reduction in rank of the required subspace and makes this method practically feasible. Further, this method retains the herglotz properties of the configuration-averaged Green function. The coupling to the recursion method allows effects of quite large clusters to be taken into account. Since the recursion method is intrinsically multisite, off-diagonal disorder and the multisite nature of the LMTOs is not a problem. Full charge self-consistency is a part of the method and we do not have to resort to the not completely satisfactory arguments of Kudrnovský and Drchal [2].

The starting point of our analysis is the most localized, sparse tight-binding Hamiltonian derived systematically from the LMTO-ASA theory and generalized to random alloys, given by

$$\begin{aligned} H^{\alpha}_{RL,R'L'} &= \hat{C}_{RL}\delta_{RR'}\delta_{LL'} + \hat{\Delta}^{1/2}_{RL} S^{\alpha}_{RL,R'L'} \hat{\Delta}^{1/2}_{R'L'} \\ \hat{C}_{RL} &= C^{\mathrm{A}}_{RL} n_R + C^{\mathrm{B}}_{RL}(1-n_R) \\ \hat{\Delta}^{1/2}_{RL} &= (\Delta^{1/2}_{RL})^{\mathrm{A}} n_R + (\Delta^{1/2}_{RL})^{\mathrm{B}}(1-n_R). \end{aligned} \tag{1}$$

Here R denotes the lattice sites and $L = (lm)$ is the orbital index (for transition metals $l \leqslant 2$). C^{A}_{RL}, C^{B}_{RL}, Δ^{A}_{RL} and Δ^{B}_{RL} are potential parameters of the constituents A and B of the alloy. To start with we take the pure elemental values available [7]. n_R are local site-occupation variables which randomly take values 0 or 1 according to whether the site is occupied by an A atom or not. The screened or tight-binding structure constant S^{α} contains all the information on lattice geometry, and it is expressed in terms of the conventional structure constant S^0 and the screened parameter α as

$$S^{\alpha} = S^0(1+\alpha S^{\alpha}) = \alpha^{-1}(\alpha^{-1} - S^0)\alpha^{-1} - \alpha^{-1}. \tag{2}$$

The Hamiltonian described by equation (1) is related to the nearly orthonormal representation (γ) by the relation

$$H^{\gamma} = E_{\nu} + h^{\gamma} = E_{\nu} + h^{\alpha} - h^{\alpha} o^{\alpha} h^{\alpha} + \ldots. \tag{3}$$

Usually the expansion is truncated after the second term which is accurate to first order in $(E - E_{\nu})$. The third term is necessary for systems with wide bands specially for s, p states. We have used both the first-order and second-order approximations. For very small energy difference calculations in the study of phase diagrams, it is essential to go beyond the first-order approximation to maintain accuracy. Once we have defined the Hamiltonian, the electronic structure is described by the configurationally averaged resolvent $\langle G(z)\rangle = \langle (zI - H)^{-1}\rangle$.

We note that the Hamiltonian has both diagonal and off-diagonal disorder. We will retain this form of the Hamiltonian, to calculate the configuration-averaged resolvent, and will not resort to any transformation as is done in single-site approximations [2]. In order to evaluate the configuration average we will employ the ideas of the ASF. The ASF puts configuration

† A system of N sites with binary distribution has a configuration space of rank 2^N.

averaging on the same footing as quantum mechanical averaging by augmenting the Hilbert space spanned by the wavefunctions with a configuration space spanned by the different realizations of random variables associated with the Hamiltonian. Let us suppose that the Hamiltonian describing the system is characterized by a set of random variables $\{x_i\}$, which are independent. The probability density of $\{x_i\}$ is assumed to have finite moments of all orders, so that we may write

$$p(x_i) = \frac{1}{\pi}\langle\gamma_0^i|((x+\mathrm{i}0)-\tilde{M}_i)^{-1}|\gamma_0^i\rangle \tag{4}$$

where $\tilde{M}_i$ is an operator defined on the configuration space ϕ_i of rank N, spanned by the N possible realizations of x_i. The augmented-space theorem now states that the configuration average of the resolvent $G(E,\{x_i\})$ may be written as

$$\langle G(E,\{x_i\})\rangle = \int G(E,\{x_i\})\prod p(x_i)\,\mathrm{d}x_i = \langle F|\left(z\tilde{I}-\tilde{H}(\{\tilde{M}_i\})\right)^{-1}|F\rangle. \tag{5}$$

$\tilde{H}(\{M_i\})$ is the same operator function in the augmented space of $\tilde{M}_i$ as $H(\{n_i\})$ was of n_i. $|F\rangle = \prod\otimes|\gamma_0^i\rangle$ is the configuration *ground state* in augmented space. Thus the configuration averaging has been reduced to the problem of the *ground state* matrix element in the augmented space $\psi = H\otimes\phi$. For a system with N sites and disorder described by binary probability distribution the rank of the space is $N\times 2^N$.

The construction of $\tilde{M}_i$ given the distribution of n_i was described in detail earlier. For a binary distribution with probabilities x_A and x_B, $\tilde{M}_i$ is

$$\begin{pmatrix} x_A & \sqrt{x_A x_B} \\ \sqrt{x_A x_B} & x_B \end{pmatrix}.$$

The configuration space is characterized by two states, which may be identified with the up and down states of an Ising system. The form of $\tilde{M}_i$ suggests that the diagonal elements are projection operators while the off-diagonal elements are *spin-flip* operators. The configuration states may then be stored extremely efficiently in bits of words and the algebra of the Hamiltonian in the configuration space may mirror the multispin coding techniques used in numerical work with the Ising model.

The augmented-space Hamiltonian for the TB-LMTO basis can be expressed as

$$\begin{aligned}\tilde{H} = {} & \sum_i\sum_L C_L^B a_{iL}^\dagger a_{iL} + \sum_{iL}\sum_{k=\uparrow,\downarrow}\sum_{k'=\uparrow,\downarrow}\delta C_L \tilde{M}_{kk'}^i b_k^{(i)\dagger} b_{k'}^{(i)} a_{iL}^\dagger a_{iL} + \dots \\ & + \sum_i\sum_L\sum_j\sum_{L'}\sum_{k_1=\uparrow,\downarrow}\sum_{k_2=\uparrow,\downarrow}\sum_{k_3=\uparrow,\downarrow}\sum_{k_4=\uparrow,\downarrow}(\Delta_L^B\dots+\delta\Delta_L\tilde{M}_{k_1,k_2}^i b_{k_1}^{(i)\dagger} b_{k_2}^{(i)}) \\ & \dots S_{iL,jL'}^\alpha(\Delta_L^B+\delta\Delta_L\tilde{M}_{k_3,k_4}^j b_{k_3}^{(j)\dagger} b_{k_4}^{(j)}) a_{iL}^\dagger a_{jL'}.\end{aligned}$$

$\delta C_L = C_L^A - C_L^B$ and $\delta\Delta_L = \Delta_L^A - \Delta_L^B$. The $a^\dagger$ and a are creation and annihilation operators in the real space and $b^\dagger$ and b are creation and annihilation operators in the configuration space, whose diagonal combination resembles S_i^z and off-diagonal combinations the spin-flip $S_i^\pm$ in a Ising model.

It is well known that for a system described by a sparse Hamiltonian the recursion method of Haydock, Heine and Kelly is one of the widely used methods to calculate the resolvent of the Hamiltonian. This method tridiagonalizes the system Hamiltonian with the aid of the recursion relation given by

$$b_{n+1}|\phi_{n+1}\rangle = H|\phi_n\rangle - a_n|\phi_n\rangle - b_n|\phi_{n-1}\rangle \tag{6}$$

where the a_n and b_n are the diagonal and off-diagonal elements of the tri-diagonalized Hamiltonian. The advantage of this method lies in the fact that the resolvent of the system

can be expressed as a continued fraction involving a_n and b_n. In practice the continued fraction is evaluated to a finite number of steps. Haydock [8] has mapped the contribution to the continued fraction coefficients to self-avoiding walks on the underlying space. He has shown that the dominant contribution comes from walks that wind round the initial starting point. This allows us to work only on a finite part of the augmented space: a particular sized cluster around the initial starting site. The continued fraction is then complemented after the finite number of steps N with a suitable terminator. The terminator reflects the asymptotic properties of the continued fraction expansion of the Green function accurately. Several terminators are available in the literature and we have chosen to use the terminator of Lucini and Nex [9]. The advantage of such a termination procedure is that the approximate resolvent retains the herglotz properties. It preserves the first $2(N-2)$ moments of the density of state exactly. This represents the effect of a cluster at distance $(N-2)$ from the starting state. It also maintains the correct band widths, band weights and the correct singularities at the band edges. It is worth mentioning that for the tight-binding Hamiltonian, the recursion method has a workload proportional to the size of the system instead of the cubic proportionality of the usual band-structure supercell method, where self-consistency is usually achieved in one k-point. From the discussion in the preceeding section, it is clear that the recursion method defined on the augmented space allows one to compute the configuration-averaged Green function directly. The method does not involve single-site approximation or solution of any self-consistent equation as required in the CPA or its generalizations.

In spite of its immense potential the method could not be used for practical calculations because of the large dimension of the augmented space†. One of the main contributions of the present communication is to devise an efficient method which systematically reduces the rank of the augmented space and thereby helps to implement augmented-space recursion for any practical calculation. Our method is based on the symmetry of the Hamiltonian in the augmented space and the multi-spin coding technique. Taking the advantage of symmetries in a Hamiltonian we can save time and storage in computation. The Hamiltonian described by equation (1) contains the information of both the structure of the underlying lattice and the symmetry of the orbitals. It has been proved by Gallagher [10] that if the starting state of the recursion belongs to an irreducible representation of the Hamiltonian, then the states generated by the process of recursion belong to the same row of the same irreducible representation of the Hamiltonian. One needs to retain only those states for the purpose of recursion and obtain the same resolution as with all of them. Thus, in computation one needs far less storage and time because the dimensionality of the matrix $\tilde{H}$ is reduced drastically. Further, the recursions with the starting states corresponding to the different rows of the same irreducible representation are similar. Also the states belonging to the different irreducible representations or different rows of the same irreducible representation do not mix. In order to facilitate such a calculation the recursion should be done only with these states, which are not related to each other by the point-group symmetry of the underlying lattice. The symmetry of the orbitals is reflected in the two-centred Koster–Slater integrals, which prohibit the overlap at certain positions dictated by the symmetry of the p and d orbitals. Since we will carry out the recursion with a reduced set of vectors obtained by the point-group symmetry of the lattice, the overlap at these symmetric positions does not cancel, and we have to explicitly supress their contribution in the Hamiltonian. Once the state vectors are identified, the recursion can be performed in the reduced space, with suitable weight factors. This method of exploiting the real-space symmetry could easily be

† $N \times 2^N$ for a system with N sites and disorder characterized by binary probability distribution.

extended to augmented space. As discussed earlier the augmented space is a direct product of the real space and the configuration space which are disjoint. As a consequence the symmetry operations apply independently to each of them. The configuration space also has a very high degree of symmetry. For example, if a site is occupied by an A atom, then all the Z configurations in which its $Z-1$ neighbours are occupied by A and one by B are equivalent. Again the symmetry of the orbitals also rules out the operation of the Hamiltonian at certain symmetric positions discussed earlier. Once the vectors are identified the recursion can be done in the reduced augmented space. We shall discuss the reduction in detail in a subsequent communication [11]. We give here a summary of the reduction procedure.

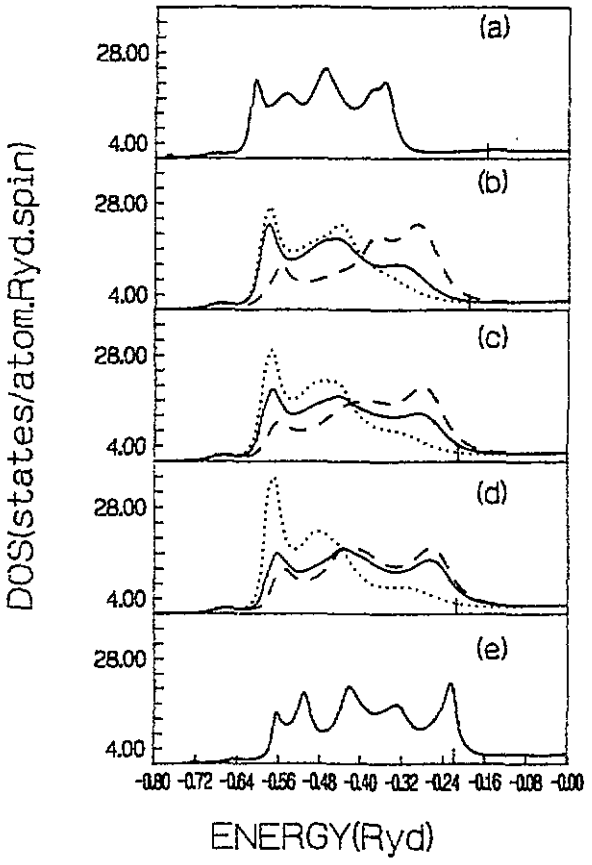

Figure 1. The total (solid) and partial densities of states on Ag (dotted) and Pd (dashed) in Ag_xPd_{1-x} alloys. The concentrations are from top to bottom $x = 1.0$, 0.75, 0.5, 0.25 and 0. The vertical lines show the positions of the Fermi energy.

A basis in the full augmented space for a binary random system is characterized by a site on the real lattice, i, a string of zeroes and ones at each of the sites which describes a configuration and angular momenta labels $L = (l, m)$. This string can be stored in bits of a word. The sequence of 1s $\{\sigma\}$ in this string completely describes the configuration and is called the *cardinality sequence*. If R_k is one of W operators which take a given site i on the lattice to one of the W equivalent positions on the lattice, then the irreducible subspace

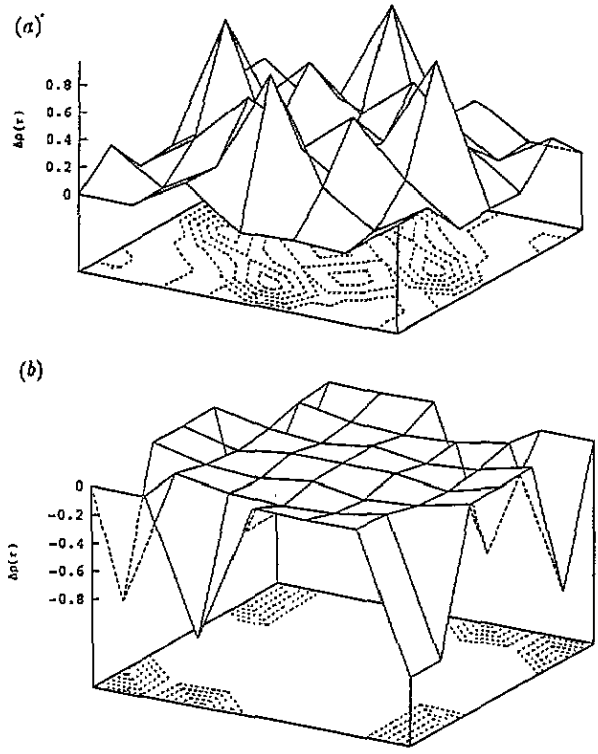

Figure 2. Differences in charge densities in an atomic sphere around (a) Pd, between Pd in the alloy and pure Pd, and (b) Ag, between Ag in the alloy and pure Ag.

is spanned by the basis

$$|i', \{\sigma'\}, L] = \left(\frac{1}{\sqrt{N}}\right) \sum_{k=1}^{N} \beta_{i'L} |R_k i', \{R_k \sigma'\}, L\rangle. \tag{7}$$

Here i' is limited to being in the positive octant and the σ' sequence contains sites only in the positive octant. The factor $\beta_{i'L}$ is the sign of the Slater–Koster function $K_{LL'}(i' - 0)$ which regulates whether the linear combination has s, p or d symmetry with respect to the origin. The irreducible representation of the Hamiltonian is

$$[j', \{\sigma_1\}, L|\tilde{H}|i'\{\sigma_2\}, L'] = \sqrt{W_R/W_L}\,\gamma\, \tilde{H}_{j\sigma_1 L, i, \sigma_2, L'}. \tag{8}$$

W_L and W_R are the weights associated with the left and right basis. The weight of a given basis is given by $W = \sum_{k=1}^{N} \beta_{i'L}$. The weight factor γ is related to the connectivity of the site with respect to its neighbours. Sites within the octant have $\gamma = 1$ while sites on symmetry planes and lines have weights > 1, determined from their connectivity. It is easy to see that the rank of the irreducible subspace is reduced immensely and allows the recursion to become tractable even on quite small computers.

In figure 1 we present calculations for AgPd alloys with varying concentration of Pd from 0 to 1. AgPd is one of the simplest illustrative cases. Its disorder is dominated by the diagonal terms in the Hamiltonian. Both constituents have roughly the same d-band widths. Since they belong to the same row of the Periodic Table, they have very little mismatch in atomic sizes. The alloy remains FCC throughout the concentration range. For the pure

metallic cases we have gone up to fifteen levels in the continued fraction to reproduce the sharp structure. For the other concentrations we have gone up to seven recursion levels. This is sufficient, since disorder smears out the fine structure in the density of states. The results are in excellent agreement with earlier LMTO-CPA results of Kudrnovský and Drchal [2], as well as the KKR-CPA results of Winter and Stocks [12]. Although, the charge self-consistency cycle is a part of this formalism (as in the LMTO and KKR), the CPA self-consistency cycle for *each* energy is avoided using the recursion and its terminators. Figure 2 shows the difference in charge densities in atomic spheres around Pd and Ag, between the charge densities in Pd and Ag in the disordered alloy and pure Pd and Ag respectively. There is clear evidence of a small charge transfer from the Ag sphere into that of Pd. The main purpose of this paper is to demonstrate that the ASF recursion can reproduce known results with controlled accuracy. The error analysis of the recursion technique is well established and allows us to introduce approximations into the terminator with controlled accuracy. We have shown, in our earlier work on model systems, that the ASF handles diagonal and off-diagonal disorder with equal facility. We shall now go ahead to apply this method to systems with local lattice distortions and short-range ordering, which lead to essential off-diagonal disorder, and which cannot be satisfactorily accounted for in the established CPA methods.

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