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Generalized augmented-space theorem for correlated disorder and the cluster-coherent-potential approximation

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We present a method for calculating the electronic structure of disordered alloys with short-range order (SRO) which guarantees a positive density of states for all values of the SRO parameter. The method is based on the generalized augmented-space theorem which is valid for alloys with SRO. This theorem is applied to alloys with SRO in the tight-binding linear-muffin-tin-orbital (TB-LMTO) framework. This is done by using the augmented-space formulation of Mookerjee and the cluster-coherent-potential approximation. As an illustration, the method is applied to a single-band model TB-LMTO Hamiltonian. We find that the SRO can induce substantial changes in the density of states.

I. INTRODUCTION

During the last two decades a good deal of progress has been made in understanding the electronic structure of random disordered alloys using the coherent potential approximation (CPA).[1-3] However, most disordered alloys have a certain degree of short-range order (SRO) which cannot be studied using the CPA since it is a single site theory.[4] The inclusion of the SRO is a challenging problem since it requires a self-consistent theory which goes beyond the CPA, i.e., one has to develop a theory which includes correlations between different sites and retains the Herglotz property of the averaged Green's function. Such a development is important not only for studying ordering and clustering in alloys, but also for developing analytic mean-field theories of liquid and amorphous materials.[2]

During the last few years, we have developed a theory for random disordered alloys in the Korringa-Kohn-Rostoker (KKR) and tight-binding linear-muffin-tin-orbital (TB-LMTO) frameworks, which goes beyond the CPA and includes correlations between different sites using the cluster coherent potential approximation (CCPA).[5-10] This theory is based on the augmented-space formulation (ASF) of Mookerjee[11,12] and guarantees a positive density of states.[9] However, inclusion of the SRO in this theory became difficult because the original augmented-space theorem is valid only for random alloys. The best one could do was to expand the averaged Green's function of the disordered alloy with SRO in terms of the averaged Green's function of the random alloy.[4] This expansion, which contained an infinite number of terms, had to be truncated for numerical calculations. Although the full expansion of the averaged Green's function was Herglotz, the truncation of the expansion sometimes gave a negative density of states for large values of the SRO parameter.

In this paper, we present another method for calculating the electronic structure of disordered alloys with SRO which does not use the expansion of the Green's function as used in the previous paper[4] and guarantees a positive density of states for all values of the SRO parameter. The first attempt to include SRO in the ASF was that of Kaplan and Gray[13] using the empirical tight-binding Hamiltonian. For construction of certain operators in the augmented space, we have followed an approach similar to theirs and have given a proof of the *generalized augmented-space theorem* in Sec. II. Although the theorem was quoted in Ref. 13, its generalization is nontrivial and a proof of the equality of the configuration average with a particular matrix element in the augmented space is essential. In Sec. III, we apply this theorem to the TB-LMTO Hamiltonian of a disordered alloy with SRO and derive necessary formulas. In our method the effective medium is calculated self-consistently using the CCPA. Within the density functional theory[14] it can be made charge self-consistent also. Our approach is quite different from that of Gonis and Freeman,[15] who have used the embedded cluster method, which is a non-self-consistent approach. In Sec. IV, we apply the formulation to an s-band alloy in the TB-LMTO framework and present the results for the density of states for several values of the SRO parameter. In Sec. V we give our conclusions.

II. THE AUGMENTED-SPACE THEOREM FOR CORRELATED VARIABLES

We shall consider a function $\mathcal{F}(\{n_i\})$ of many variables $\{n_i\}$ which are random but have correlations built into their behavior. The average of the function over all possible *configurations* of this random set is given by[5,11]:

$$\langle\mathcal{F}(\{n_i\})\rangle = \int\int\cdots\int dn_1 dn_2\cdots dn_k\cdots\mathcal{F}(\{n_i\}) \times P(n_1,n_2,\ldots,n_k,\ldots)\,. \quad (1)$$

Unlike the case of independent random variables, the joint probability distribution, $P(n_1,n_2,\ldots,n_k,\ldots)$, does not break up into individual probability densities. However, we may rewrite the above equation in terms of *conditional* probability densities $p_1(n_1)$, $p_2(n_2|n_1)$, etc.,[13]

$$\langle \mathcal{F}(\{n_i\})\rangle = \int\int\cdots\int dn_1 dn_2\cdots dn_k\cdots \mathcal{F}(\{n_i\}) \times p_1(n_1)p_2(n_2|n_1)p_3(n_3|n_2,n_1)\cdots p_k(n_k|n_{k-1},n_{k-2},\cdots,n_1)\cdots \,. \tag{2}$$

We notice that each of the conditional probability densities has the positive definiteness necessary for the augmented-space theorem to hold. In addition we also impose finiteness to all the moments of these densities, in order to avoid difficult convergence problems. This restriction is not stringent, since almost all the physical conditional probability densities obey this restriction anyway.

We shall first describe construction of operators associated with each of the probability densities and subsequently give a proof of the *generalized augmented-space theorem* regarding the configuration average of the type shown in Eq. (1). We start with the unrestricted probability density $p_1(n_1)$. We associate with this an operator M_1 such that

$$p_1(n_1) = -(1/\pi)\mathrm{Im}\langle f_1^0|(n_1 I - M_1)^{-1}|f_1^0\rangle \,. \tag{3}$$

Given the probability density, the construction of a representation of the operator has been described in some detail by Mookerjee.[11] Here we wish to remark on some relevant properties of this operator. The operator is a mapping on the *configuration space* of the variable n_1. Corresponding to the various values m_1^k randomly assumed by n_1, we may assign states $|m_1^k\rangle$ to our system. The space spanned by these states is the *configuration space* ϕ_1 associated with the variable n_1. The rank of this space, as well as the rank of the operator M_1, is the number of different values which n_1 can assume. From the relationship between the resolvent of M_1 and the probability density, we can immediately conclude that the states corresponding to definite values attained by n_1 are eigenstates of the operator M_1 with eigenvalues m_1^k. Let ω_k be the statistical weight associated with the value m_1^k. From Eq. (2) we can find that[11]

$$\langle n_1\rangle = \langle f_1^0|M_1|f_1^0\rangle = \sum_k m_1^k \omega_k \,. \tag{4}$$

The alternative basis $\{|f_1^j\rangle\}$ has been constructed as a linear combination of the eigenbasis with

$$|f_1^0\rangle = \sum_k \sqrt{\omega_k}|m_1^k\rangle \,.$$

For a binary distribution of n_1, e.g., taking two values n_A and n_B, the transformation matrix connecting the eigenbasis to the basis $|f_1^j\rangle$ is given by

$$U = \begin{pmatrix} \sqrt{\omega_A} & \sqrt{\omega_B} \\ \sqrt{\omega_B} & -\sqrt{\omega_A} \end{pmatrix} \,. \tag{5}$$

Thus $U^\dagger M_1 U$ is diagonal, with elements n_A and n_B. We shall also define a set of projection operators, P_1^k, which project onto the eigenstates of M_1. In the eigenbasis these operators have representation matrices which are zero everywhere except at the kth diagonal position. We may easily find their representation in the basis $\{|f_1^j\rangle\}$ by premultiplying and postmultiplying by the transformation matrix U. For the binary case, for example, we have

$$P_1^A = \begin{pmatrix} \omega_A & \sqrt{\omega_A\omega_B} \\ \sqrt{\omega_A\omega_B} & \omega_B \end{pmatrix} \,,$$

$$P_1^B = \begin{pmatrix} \omega_B & -\sqrt{\omega_A\omega_B} \\ -\sqrt{\omega_A\omega_B} & \omega_A \end{pmatrix} \,. \tag{6}$$

The full configuration space consists of the product of the individual configuration spaces of each of the variables, i.e,

$$\Phi = \prod_n \otimes\phi_n \,.$$

We now extend the operator M_1 onto the full configuration space by

$$\tilde{M}_1 = M_1 \otimes I \otimes I \otimes \cdots \,.$$

Let us now come to the variable n_2. For this, we have several distinct conditional probability densities, depending on the value taken by the variable n_1. For each value m_1^k taken by n_1, we associate with the corresponding *conditional* probability density $p_2(n_2|n_1=m_1^k)$ an operator M_2^k, such that

$$p_2(n_2|n_1=m_1^k) = (-1/\pi)\mathrm{Im}\langle f_2^0|(n_2 I - M_2^k)^{-1}|f_2^0\rangle \,. \tag{7}$$

The operator $\tilde{M}_2$ we wish to associate with the variable n_2 should be that M_2^k which corresponds to the particular configuration m_1^k which n_1 takes. A natural generalization then takes the form

$$\tilde{M}_2 = \sum_k P_1^k \otimes M_2^k \otimes I \otimes \cdots \,.$$

When we come to the next variable n_3, there are now different *conditional* probabilities $p_3(n_3|n_2=m_2^{k_2}, n_1=m_1^{k_1})$ depending on the different configurations attained by *both* the variables n_1 and n_2. With each one of these we now associate an operator $M_3^{k_1,k_2}$. Using the same type of argument as in the previous case, we associate an operator $\tilde{M}_3$ with the variable n_3, given by

$$\tilde{M}_3 = \sum_{k_1}\sum_{k_2} P_1^{k_1} \otimes P_2^{k_2} \otimes M_3^{k_1,k_2} \otimes I \otimes \cdots \,.$$

We go on associating operators $\tilde{M}_p$ with each of the variables n_p in turn. In general,

$$\tilde{M}_p = \sum_{k_1}\cdots\sum_{k_{p-1}} P_1^{k_1} \otimes P_2^{k_2} \cdots \otimes M_p^{k_1,k_2\cdots k_{p-1}} \otimes I \otimes \cdots \,.$$

Having done this, we now wish to prove the central theorem.

Theorem. The configuration average of the function $\mathcal{F}(\{n_i\})$ is given by $\langle F^0|\tilde{\mathcal{F}}(\{\tilde{M}_i\})|F^0\rangle$, where $|F^0\rangle = \prod_i \otimes |f_i^0\rangle$.

Proof. Let us first note that

$$P_n^k P_n^{k'} = \delta_{kk'} P_n^k \, . \tag{8}$$

Let $m_p^{k_p}$ denote the eigenvalues of $M_p^{k_1,k_2\cdots k_{p-1}}$ with statistical weights equal to $\omega_{k_p}^{k_1,k_2\cdots k_{p-1}}$. Then we note that we can expand

$$|f_p^0\rangle = \sum_{k_p} \sqrt{\omega_{k_p}^{k_1,k_2\cdots k_{p-1}}}\,|m_p^{k_p}\rangle$$

and

$$M_p^{k_1,k_2\cdots k_{p-1}}\; P_p^{k_p}|f_p^0\rangle = M_p^{k_1,k_2\cdots k_{p-1}} \sqrt{\omega_{k_p}^{k_1,k_2\cdots k_{p-1}}}\,|m_p^{k_p}\rangle . \\ = m_p^{k_p} \sqrt{\omega_{k_p}^{k_1,k_2\cdots k_{p-1}}}\,|m_p^{k_p}\rangle \, ,$$

so that

$$\langle f_p^0|M_p^{k_1,k_2\cdots k_{p-1}} P_p^{k_p}|f_p^0\rangle = m_p^{k_p}\omega_{k_p}^{k_1,k_2\cdots k_{p-1}} \, . \tag{9}$$

Since $|m_p^{k_p}\rangle$ are eigenfunctions of $M_p^{k_1,k_2\cdots k_{p-1}}$, a simple generalization will give us

$$\langle f_p^0|\left[M_p^{k_1,k_2\cdots k_{p-1}}\right]^r P_p^{k_p}|f_p^0\rangle = \left[m_p^{k_p}\right]^r \omega_{k_p}^{k_1,k_2\cdots k_{p-1}} \, , \tag{10}$$

where r is an integer.

Consider now the following relationship:

$$\langle F^0|[\tilde{M}_1]^{r_1} \otimes [\tilde{M}_2]^{r_2} \otimes \cdots |F^0\rangle = \langle F^0|\tilde{M}_1^{r_1} \left[\sum_{k_1} P_1^{k_1} \otimes \left(M_2^{k_1}\right)^{r_2} \otimes I \cdots\right] \\ \times \left[\sum_{k_1',k_2} P_2^{k_1'} \otimes \mathrm{P}_{k_2} \otimes \left(M_3^{k_1',k_2}\right)^{r_3} \otimes \cdots\right] \cdots |F^0\rangle \, .$$

If we now expand the terms in the brackets and gather terms together, we get

$$\sum_{k_1}\sum_{k_1'}\cdots\sum_{k_1''}\left[(\tilde{M}_1)^{r_1} P_1^{k_1} P_1^{k_1'} \cdots P_1^{k_1''}\right] \otimes \sum_{k_2}\sum_{k_2'}\cdots\sum_{k_2''}\left[(\tilde{M}_2^{k_1})^{r_2} P_2^{k_2} P_2^{k_2'} \cdots P_2^{k_2''}\right] \otimes \cdots \, .$$

Using Eq. (8), the relevant δ functions reduce all multiple summations per variable label to only one per label and only one projection operator per label survives in the above expression and we get

$$\sum_{k_1} (\tilde{M}_1)^{r_1} P_1^{k_1} \otimes \sum_{k_2} (\tilde{M}_2^{k_1})^{r_2} P_2^{k_2} \otimes \cdots \, .$$

Now taking the matrix elements between $|F^0\rangle$ and using (10) we get

$$\sum_{k_1}\sum_{k_2}\cdots (m_1^{k_1})^{r_1} (m_2^{k_2})^{r_2} \cdots \omega_{k_1}\omega_{k_2}^{k_1}\omega_{k_3}^{k_1,k_2} \cdots \, .$$

By definition, it is easy to see that this is $\langle n_1^{r_1} n_2^{r_2} \cdots\rangle$.

Finally we define a well-behaved operator function $\tilde{\mathcal{F}}(\{\tilde{M}_i\})$ of the operators $\{\tilde{M}_i\}$ as the series

$$\tilde{\mathcal{F}}(\{\tilde{M}_i\}) = \sum_{r_1}\sum_{r_2}\cdots\sum_{r_p} B_{r_1,r_2\ldots} \tilde{M}_1^{r_1}\tilde{M}_2^{r_2} \cdots \, .$$

Using the result already proved above, we obtain

$$\begin{aligned}
\langle F^0|\tilde{\mathcal{F}}(\{\tilde{M}_i\})|F^0\rangle &= \sum_{r_1}\sum_{r_2}\cdots B_{r_1,r_2\ldots} \langle F^0|\tilde{M}_1^{r_1}\tilde{M}_2^{r_2}\cdots|F^0\rangle \\
&= \sum_{r_1}\sum_{r_2}\cdots\sum B_{r_1,r_2\ldots}\cdots \\
&\quad \cdots\sum_{k_1}\sum_{k_2}\cdots\sum (m_1^{k_1})^{r_1}(m_2^{k_2})^{r_2}\cdots\omega_{k_1}\omega_{k_2}^{k_1}\omega_{k_3}^{k_1,k_2}\cdots \\
&= \sum_{k_1}\sum_{k_2}\cdots\omega_{k_1}\omega_{k_2}^{k_1}\omega_{k_3}^{k_1,k_2}\cdots \\
&\quad \cdots\sum_{r_1}\sum_{r_2}\cdots B_{r_1,r_2\ldots}(m_1^{k_1})^{r_1}(m_2^{k_2})^{r_2}\cdots \\
&= \sum_{k_1}\sum_{k_2}\cdots\omega_{k_1}\omega_{k_2}^{k_1}\omega_{k_3}^{k_1,k_2}\cdots\mathcal{F}(m_1^{k_1},m_2^{k_2}\cdots) \, .
\end{aligned}$$

From definition this is the configuration average $\langle \mathcal{F}(n_1, n_2 \cdots) \rangle$.

This completes the proof of the *generalized augmented-space theorem.*

III. THE TB-LMTO AND THE CLUSTER-COHERENT-POTENTIAL APPROXIMATION

The tight-binding or screened version of the linearized-muffin-tin-orbitals method (TB-LMTO) has provided an excellent starting point for first-principles electronic structure determination of disordered alloys. The resulting Hamiltonian is short-ranged and therefore ideally provides the extension from the traditional *ad hoc* tight-binding ideas into a fully-self-consistent first-principles theory. The basis of the method has been described in detail by Andersen[16] and relevant details necessary for disordered alloys are given in Refs. 8 and 17. Here we shall quote only some of the principal results necessary for our discussion.

We shall be using the most localized TB-LMTO representation called β representation. In this paper, we shall focus on a binary substitutional disordered alloy of A and B atoms. Let R denote an atomic position and L a collective angular momentum index for (l, m). The scattering properties of the potentials are characterized by the potential parameters C_{RL}, Δ_{RL}, and γ_{RL}. Kudrnovský and Drchal[17] have rewritten the Green's function of the system in terms of site-diagonal random functions $\lambda^{\beta}_{RL}(z)$ and $\mu^{\beta}_{RL}(z)$, which are functions of the potential parameters, and an auxiliary Green's function $g^{\beta}_{RL,R'L'}(z)$,

$$G_{RL,R'L'}(z) = \lambda^{\beta}_{RL}(z)\delta_{RR'}\delta_{LL'} + \mu^{\beta}_{RL}(z) g^{\beta}_{RL,R'L'}(z) \mu^{\beta}_{R'L'}(z) \;, \tag{11}$$

with

$$g^{\beta}_{RL,R'L'}(z) = (\mathcal{A}^{-1})_{RL,R'L'} \;, \tag{12}$$

where

$$\mathcal{A}_{RL,R'L'} = \left\{ \left[P^{\beta}(z) - S^{\beta} \right]^{-1} \right\}_{RL,R'L'} \;. \tag{13}$$

The potential functions $P^{\beta}_{RL}(z)$ are random and site-diagonal but the screened structure functions $S^{\beta}_{RL,R'L'}$ are nonrandom if there is no structural disorder. The potential function has a binary distribution and may be written in terms of random *occupation* variables $\{n_R\}$ which take the values 1 if the site R is occupied by an atom of the type A and 0 if it is not. The probability weights associated with the variables will, of course, depend upon whether we wish to incorporate SRO or not.

Our first task would be to obtain a CCPA for the configuration average of the auxiliary Green's function, $g^{\beta}_{RL,R'L'}(z)$. For this we follow a procedure very similar to that of Razee and Prasad.[8] We shall first consider the auxiliary Hamiltonian $\mathcal{A}$ written as an operator in a Hilbert space H spanned by the site-angular momentum labeled TB-LMTO basis.

$$\begin{aligned} \mathcal{A} &= \sum_R P^{\beta}_R |R\rangle\langle R| - \sum_R \sum_{R'} S^{\beta}_{RR'} |R\rangle\langle R'| \;, \\ &= P^{\beta,B} \sum_R |R\rangle\langle R| + \delta P \sum_R |R\rangle \\ &\quad \times \langle R| n_R - \sum_R \sum_{R'} S^{\beta}_{RR'} |R\rangle\langle R'| \;, \end{aligned} \tag{14}$$

where

$$\delta P = P^{\beta,A} - P^{\beta,B} \;,$$

and we have suppressed the angular momentum index L for convenience. As described in the earlier section, we may now associate with various site occupation variables n_R corresponding operators $\tilde{M}_R$ in the configuration space of the random variables. We notice that[4]

$$p(n_{R_1}) = x\delta(n_{R_1} - 1) + y\delta(n_{R_1}) \;,$$

$$p(n_{R_2}|n_{R_1} = 1) = (x + \alpha y)\delta(n_{R_2} - 1) + (1 - \alpha)y\delta(n_{R_2}) \;,$$

$$p(n_{R_2}|n_{R_1} = 0) = (1 - \alpha)x\delta(n_{R_2} - 1) + (y + \alpha x)\delta(n_{R_2}) \;.$$

Here x and y are the concentrations of the A and B constituents and α is the Warren-Cowley SRO parameter.[4] Note that $\alpha = 0$ when there is no SRO and the conditional probabilities of the second variable become identical and equal to the unrestricted probability density of the first variable. $\alpha < 0$ indicates a tendency towards ordering, while $\alpha > 0$ indicates a tendency towards segregation. The representations of the different operators associated with the variables, discussed in the earlier section, are

$$M_1 = \begin{pmatrix} x & \sqrt{xy} \\ \sqrt{xy} & y \end{pmatrix} \;,$$

$$M_2^1 = \begin{pmatrix} x + \alpha y & \sqrt{(1-\alpha)y(x+\alpha y)} \\ \sqrt{(1-\alpha)y(x+\alpha y)} & (1-\alpha)y \end{pmatrix} \;,$$

$$M_2^0 = \begin{pmatrix} (1-\alpha)x & \sqrt{(1-\alpha)x(y+\alpha x)} \\ \sqrt{(1-\alpha)x(y+\alpha x)} & y + \alpha x \end{pmatrix} \;,$$

$$P_1^1 = \begin{pmatrix} x & \sqrt{xy} \\ \sqrt{xy} & y \end{pmatrix} \;,$$

$$P_1^0 = \begin{pmatrix} y & -\sqrt{xy} \\ -\sqrt{xy} & x \end{pmatrix} \;. \tag{15}$$

In this representation, the operators associated with the sites R_1 and R_2 operate *only* on the configuration spaces of the respective variables. These configuration spaces are of rank 2, as the operators described above. We have to generalize these operators on the full configuration space of the alloy in a manner described in the earlier section. Let us introduce projection and transfer operators in the configuration space ϕ_n :

$$\mathcal{P}_n^0 = |f_n^0\rangle\langle f_n^0|; \mathcal{T}_n^{01} = |f_n^0\rangle\langle f_n^1| \,.$$

In terms of these, the two operators $\tilde{M}_1$ and $\tilde{M}_2$ may be written as

$$\tilde{M}_1 = \left[x\mathcal{P}_1^0 + y\mathcal{P}_1^1 + \sqrt{(xy)}(\mathcal{T}_1^{01} + \mathcal{T}_1^{10})\right] \otimes I \otimes \cdots \tag{16}$$

$$\begin{aligned}\tilde{M}_2 = [&x\mathcal{P}_1^0 \otimes \mathcal{P}_2^0 + y\mathcal{P}_1^0 \otimes \mathcal{P}_2^1 + X\mathcal{P}_1^1 \otimes \mathcal{P}_2^0 + X'\mathcal{P}_1^1 \otimes \mathcal{P}_2^1 + B_1\mathcal{P}_1^0 \otimes (\mathcal{T}_2^{01} + \mathcal{T}_2^{10}) \\ &+B_2\mathcal{P}_1^1 \otimes (\mathcal{T}_2^{01} + \mathcal{T}_2^{10}) + B_3(\mathcal{T}_1^{01} + \mathcal{T}_1^{10}) \otimes \mathcal{P}_2^0 + B_4(\mathcal{T}_1^{01} + \mathcal{T}_1^{10}) \otimes \mathcal{P}_2^1 \\ &+B_5(\mathcal{T}_1^{01} + \mathcal{T}_1^{10}) \otimes (\mathcal{T}_2^{01} + \mathcal{T}_2^{10})] \otimes I \otimes \cdots \;,\end{aligned} \tag{17}$$

where

$$X = x - \alpha(x-y); X' = y + \alpha(x-y) \;,$$

$$B_1 = x\sqrt{(1-\alpha)y(x+\alpha y)} + y\sqrt{(1-\alpha)x(y+\alpha x)} \;,$$

$$B_2 = y\sqrt{(1-\alpha)y(x+\alpha y)} + x\sqrt{(1-\alpha)x(y+\alpha x)} \;,$$

$$B_3 = \alpha\sqrt{xy} \;,$$

$$B_4 = -\alpha\sqrt{xy} \;,$$

$$B_5 = \sqrt{xy}\left[\sqrt{(1-\alpha)y(x+\alpha y)} - \sqrt{(1-\alpha)x(y+\alpha x)}\right] \;.$$

We check that when α =0, i.e., when there is no SRO,

$$X = x, X' = y, B_1 = B_2 = \sqrt{xy}, B_3 = B_4 = B_5 = 0 \;,$$

reducing $\tilde{M}_2$ to a form identical to $\tilde{M}_1$, as it should be for independent random variables.

The *generalized augmented-space theorem* then leads to

$$\langle g^\beta_{R,R'}\rangle = \langle RF^0|\tilde{\mathcal{A}}^{-1}|R'F^0\rangle \;, \tag{18}$$

where

$$\tilde{\mathcal{A}} = P^{\beta,B}\sum_R |R\rangle\langle R| \otimes \tilde{I} + \delta P\sum_R |R\rangle\langle R| \otimes \tilde{M}_R - \sum_R\sum_{R'} S^\beta{}_{RR'}|R\rangle\langle R'| \otimes \tilde{I} \;. \tag{19}$$

The CCPA now proceeds in a way identical to that described for the KKR-CCPA by Razee *et al.*[5] The principal steps involve the following.

(i) Partitioning the full augmented space $\Psi = H \otimes \Phi$ into a subspace Ψ^1 spanned by the cluster $\mathcal{C}$ and its configurations. If the cluster $\mathcal{C}$ is of size N then the rank of this subspace is $N{\times}2^N$. The Hamiltonian in the rest of the augmented space is replaced by an effective, nonrandom, translationally symmetric Hamiltonian $\mathcal{A}^{\text{eff}}$, corresponding to the potential function $P^{\beta,\text{eff}}$ at each site and the structure functions $S^{\beta,\text{eff}}_{RR'}$ of the effective medium.

(ii) The Green's function in this subspace is obtained by the *partition theorem* or *downfolding*[18] into this subspace. This Green's function will therefore involve the effective Hamiltonian $\mathcal{A}^{\text{eff}}$.

(iii) We next partition this subspace into a subspace spanned by the vectors $\{|R \in \mathcal{C}F^0\rangle\}$ and its complement. Again the Green's function in this subspace is obtained by the *partition theorem* or *downfolding*.

(iv) The *generalized augmented-space theorem* then tells us that the Green's function which we have obtained, i.e.,

$$\langle R \in \mathcal{C}F^0|\tilde{\mathcal{A}}^{-1}|R \in \mathcal{C}F^0\rangle,$$

is the configuration averaged Green's function $\langle g^\beta_{RR'}\rangle$.

(v) We now choose the effective Hamiltonian $\mathcal{A}^{\text{eff}}$ such that the auxiliary Green's function for the effective medium, $\mathcal{G}^\beta_{RR'}$, is the configuration averaged Green's function obtained in (iv), i.e.,

$$\mathcal{G}^{\beta}_{RR'} = \langle g^{\beta}_{RR'} \rangle .$$

This gives us the CCPA equations for obtaining the effective Hamiltonian and hence the configuration averaged Green's function.

This procedure has been described in detail several times in different contexts. We shall refer the reader to the earlier references[5,4,8,10] and quote only those results which are modified when we introduce SRO. In Appendix A of Razee *et al.*,[5] it was shown that if we take a one-atom cluster, then the self-consistent equations reduce exactly to the traditional CPA equations. It becomes also clear that within a one-site approximation SRO cannot be logically introduced. We require at least a two-site approximation. Thus we choose our cluster $\mathcal{C}$ as consisting of two sites, $R_1 \equiv 1$ and $R_2 \equiv 2$.[19] Within this approximation, the partitioning mentioned in (i) leads to a subspace I of rank $8 = 2\times 2^2$, and after replacing $\mathcal{A}$ in the subspace II by

$$\mathcal{A}^{\text{eff}} = \mathcal{P}^{\beta,\text{eff}} \sum_R |R\rangle\langle R| - \sum_R \sum_{R'} S^{\beta,\text{eff}}_{RR'} |R\rangle\langle R'| ,$$

we get, for the matrix $\hat{A}$ [see Eq. (2.20) of Razee *et al.*,[5]] an 8×8 matrix:[20]

.	100	200	101	110	111	201	210	211
100	P_1	V	0	W	0	0	0	0
200	V	P_1	0	0	0	B'_1	B'_3	B'_5
101	0	0	P_1	0	W	V	0	0
110	W	0	0	P_2	0	0	V	0
111	0	0	W	0	P_2	0	0	V
201	0	B'_1	V	0	0	P_2	B'_5	B'_4
210	0	B'_3	0	V	0	B'_5	$\hat{P}_1$	B'_2
211	0	B'_5	0	0	V	B'_4	B'_2	$\hat{P}_2$

Here,

$$\bar{P} = (xP^{\beta,A} + yP^{\beta,B}) ,$$

$$P_1 = \bar{P} - \xi_{11} ,$$

$$P_2 = (yP^{\beta,A} + xP^{\beta,B}) - \xi_{11} ,$$

$$\hat{P}_1 = (1-\alpha)P_1 + \alpha P_2 - \xi_{11} ,$$

$$\hat{P}_2 = \alpha P_1 + (1-\alpha)P_2 - \xi_{11} ,$$

$$V = -(S^{\beta}_{12} + \xi_{12}) ,$$

$$W = \sqrt{xy}\,\delta P ,$$

$$B'_n = B_n \delta P \text{ for } n = 1, \ldots, 5 , \tag{20}$$

where $\xi_{RR'}$ are given by[8,19]

$$\xi_{11} = P^{\beta,\text{eff}} - [\mathcal{G}^{\beta}_{11} - \mathcal{G}^{\beta}_{12}(\mathcal{G}^{\beta}_{11})^{-1}\mathcal{G}^{\beta}_{21}]^{-1} ,$$

$$\xi_{12} = -S^{\beta,\text{eff}}_{12} - [\mathcal{G}^{\beta}_{12} - \mathcal{G}^{\beta}_{11}(\mathcal{G}^{\beta}_{12})^{-1}\mathcal{G}^{\beta}_{11}]^{-1} .$$

The further partitioning of this matrix as in (iii) is indicated in the above matrix itself. The augmented-space theorem then gives

$$P^{\beta,\text{eff}} = \bar{P} - \left(D^{\dagger}E^{-1}D\right)_{11} , \tag{21}$$

$$S^{\beta,\text{eff}}_{12} = S^{\beta}_{12} + \left(D^{\dagger}E^{-1}D\right)_{12} , \tag{22}$$

where

$$D = \begin{pmatrix} 0 & W & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & B'_1 & B'_3 & B'_5 \end{pmatrix} ,$$

$$E = \begin{pmatrix} P_1 & 0 & W & V & 0 & 0 \\ 0 & P_2 & 0 & 0 & V & 0 \\ W & 0 & P_2 & 0 & 0 & V \\ V & 0 & 0 & P_2 & B'_5 & B'_4 \\ 0 & V & 0 & B'_5 & \hat{P}_1 & B'_2 \\ 0 & 0 & V & B'_4 & B'_2 & \tilde{P}_2 \end{pmatrix} .$$

Equations (21) and (22) are the self-consistent CCPA equations which determine $P^{\beta,\text{eff}}$ and $S^{\beta,\text{eff}}$. It is easy to check that these equations exactly coincide with Eqs. (30) and (31) of Razee and Prasad[8] when the SRO vanishes, i.e., α=0. The above discussion allows us to completely obtain a CCPA version of the auxiliary Green's function $\langle g^{\beta}_{RR'} \rangle$. The calculation of the full Green's function average then proceeds in a way very similar to Razee and Prasad[8] and, therefore, we shall not repeat it here. From these average Green's functions, the density of states and charge density can be calculated. We note that the structure of the augmented-space Hamiltonian (19) remains the same as in the case of no SRO, the only change being in the construction of the operators $\tilde{M}_R$ associated with the random variable n_R. As a result, the proof of analyticity of the CCPA based on the ASF given earlier by Razee *et al.*[9] also carries through and the density of states is guaranteed to be positive.

IV. APPLICATION TO AN *s*-BAND ALLOY

To illustrate our formalism, we have chosen a simple *s*-band model, on a bcc lattice. The model, while computationally simple, contains essential ingredients of the realistic TB-LMTO Hamiltonian. The model has been previously used by Razee and Prasad[8] in connection with the implementation of their TB-LMTO-CCPA formulation and, therefore, we shall not repeat the details of the model here. For this calculation, we have chosen a two-atom cluster, consisting of site (0,0,0) and one of its neighboring sites (0.5,0.5,0.5). The self-consistent equations for this cluster, Eqs. (21) and (22), were solved iter-

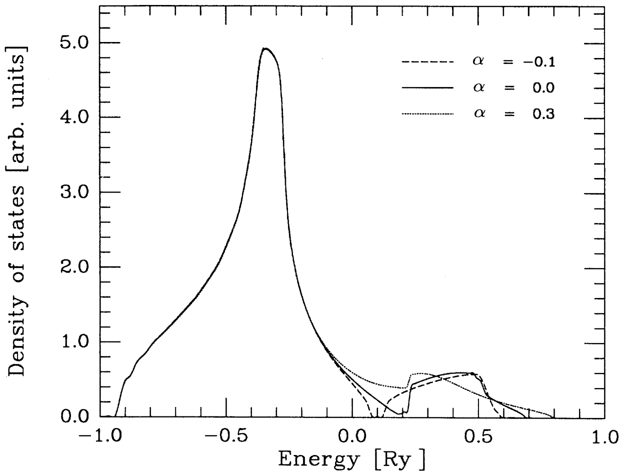

FIG. 1. Average density of states for the alloy with short range order for concentration $x = 0.9$.

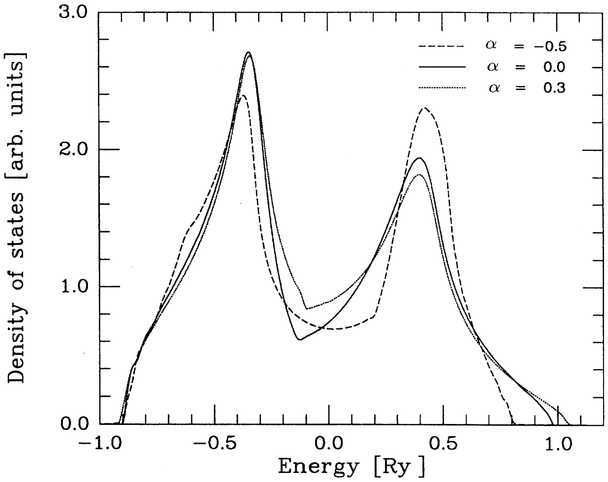

FIG. 2. Same as in Fig. 1, but for $x = 0.5$.

atively. The convergence in $P^{\beta,\mathrm{eff}}$ and $S^{\beta,\mathrm{eff}}$ was achieved within 0.001 a.u. . We have chosen the values of C, Δ, and γ as −0.75 Ry, 0.08 Ry, and 0.42 for A atoms and −0.35 Ry, 0.17 Ry, and 0.39 for B atoms, respectively. This choice corresponds to the case when both diagonal and off-diagonal disorders are present.

In Fig. 1 we show the average density of states for $x = 0.9$ for various values of the SRO parameter α. Although the majority band is not much affected by changing α, there are large changes in the impurity band. For $\alpha = -0.1$, which corresponds to the ordering tendency, the impurity band shifts to lower energies. Also there is a clear band gap between the majority band and the impurity band. In contrast, for $\alpha = 0.3$, which corresponds to a tendency towards segregation, the minority band spreads out to higher energies compared to the random case ($\alpha = 0$). Also there is a substantial density of states in the energy region, whereas for the random case the density of states is almost zero.

In Fig. 2 the average density of states for x=0.5 is shown for $\alpha = -0.5$, 0.0, and 0.3. Now we note substantial changes in both the bands. For $\alpha = -0.5$, there is a shift of weight from the lower band to the higher one, and there is a narrowing of the bands. Also, in the middle of the bands the density of states is smaller than that for the random case. For $\alpha = 0.3$, again there is a broadening of the bands and the density of states in the middle region is larger than that for the random case. Some of these trends are also visible in earlier empirical tight-binding calculations,[21,22] although the changes in bandwidths due to SRO appear to be quite small.

V. CONCLUSIONS

In this paper we have given a proof of the *generalized augmented-space theorem* which is valid in the presence of short-range order. We have applied this theorem to a TB-LMTO Hamiltonian to calculate the electronic structure of a binary substitutional disordered alloy and developed a CCPA method which guarantees positive density of states. The method was illustrated by applying it to an s-band alloy model. We found that the inclusion of SRO can change the density of states substantially. In particular, for SRO favoring ordering we find narrowing of bands, while for SRO favoring clustering there is broadening. We feel that this could lead to significant change in the total energy.

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[19] In our earlier works, Refs. 4–9, $\mathcal{C}$ consisted of sites 0 and 1.

[20] The columns in the matrix are numbered by three integers. The first indicates the site it belongs to, i.e., R_1 or R_2. The next two give the configurations of the two sites : 0 corresponding to f^0 at that site and 1 to f^1 .

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