

## Elementary excitations in random substitutional alloys\*

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A theory for elementary excitations in random substitutional alloys with off-diagonal as well as diagonal disorder has been developed using a new technique for configurational averaging introduced by Mookerjee. The theory is valid in both the long- and short-mean-free-path regions, and generates a Green's function which is always analytic. The mathematical formalism is illustrated for the case of electrons in a binary alloy with a tight-binding Hamiltonian. Typical results for the densities of states of one-dimensional chains are shown to compare well with essentially exact numerical calculations.

### I. INTRODUCTION

Since the introduction of the coherent-potential approximation (CPA) in 1967 by Soven<sup>1</sup> and Taylor,<sup>2</sup> there has been a great deal of work done on the theory of disordered systems trying to extend the CPA to include off-diagonal disorder and multi-site correlations.<sup>3-10</sup> While there have been some successes, no general theory has emerged.

A new approach to the problem of disordered systems which we believe holds great promise was introduced by Mookerjee<sup>11,12</sup> in 1973. This approach centers around a new technique for averaging functions of independent random variables. Using this technique Mookerjee was able to develop a new theory for randomly disordered alloys in which there is only site-diagonal disorder. This theory successfully includes multisite correlations and has been used to calculate the densities of electronic states for diagonally disordered one- and three-dimensional random alloys.<sup>12-14</sup> Despite his successes with this formalism, Mookerjee<sup>15</sup> was not able to properly include off-diagonal disorder. He was successful only in extending the theory to include the special case of a random bond model which, in general, is not applicable to physical systems. (The relationship of this special case to the more general off-diagonal disorder problem is discussed in Sec. II.)

In this paper we show how to extend the formalism introduced by Mookerjee to properly include off-diagonal disorder. We then discuss two computational methods based on this formalism.

The essential feature of this theory is the unique way in which configurational averages are handled. Rather than expanding the Green's function in some manner and then averaging an appropriate set of terms as is the conventional practice, we transform the random problem into an ordered one which is defined in a larger Hilbert space.

We then evaluate the Green's function in this extended space by using conventional expansion techniques.

This new Hilbert space is referred to as the augmented space. In somewhat oversimplified terms, this augmented space may be described as the direct product of the Hilbert space spanned by the original Hamiltonian with a "disorder" space which describes the various allowed configurations of the solid. On transforming to this augmented space, a new nonrandom Hamiltonian can be defined such that configurational averages in real space for the random solid are equal to inner products in the augmented space.

Once the augmented space is constructed we evaluate the Green's function in this space by applying two techniques previously used on solids with diagonal disorder<sup>12-14</sup> only: the recursion method of Haydock *et al.*<sup>16</sup> and the graphical method of Anderson.<sup>17</sup> We emphasize that although we have found these methods to be useful techniques for evaluating the Green's function, they are not essential to the basic theory. The transformation to augmented space is exact and yields a new Hamiltonian which may be treated by other means as well.<sup>18</sup>

The theory is quite general and can be applied equally well to any elementary excitations in random substitutional alloys. In order to be specific we have chosen to investigate here the electronic properties of a binary alloy. In Sec. II of this paper we review the transformation to augmented space. Sections III and IV deal with the two techniques we have chosen to use in evaluating the augmented space Green's function, the recursion method and the graphical method, respectively. For each method we include the results of calculations for one-dimensional alloys which are compared with essentially exact results. Concluding remarks are contained in Sec. V.

## II. AUGMENTED SPACE FORMALISM

In this section we describe the augmented space formalism as applied to the electronic properties of a random substitutional binary  $A$ - $B$  alloy with a nearest-neighbor, tight-binding Hamiltonian  $H$ ,

$$H_{ij} = e_i \delta_{ij} + W_{ij}. \quad (2.1)$$

The diagonal element  $e_i$  equals either  $e_A$  or  $e_B$ , and the off-diagonal element  $W_{ij}$  takes on the values  $W_{AA}$ ,  $W_{BB}$ , or  $W_{AB} = W_{BA}$  depending on the occupation of sites  $i$  and  $j$ .  $W_{ij} = 0$  if  $i = j$  or if  $i$  and  $j$  are not nearest neighbors. The relative concentrations of the  $A$  and  $B$  constituents are denoted by  $c_A$  and  $c_B = 1 - c_A$ , respectively.

We describe the configuration of the alloy in terms of a site occupation variable  $s_i$ , where  $s_i = s_A(s_B)$  if an  $A$  atom ( $B$  atom) is present at site  $i$ . For a random substitutional alloy, the  $\{s_j\}$  are independent random variables with probability distribution  $p_i(s_i)$ . For a binary alloy,

$$p_i(s_i) = c_A \delta_D(s_i - s_A) + c_B \delta_D(s_i - s_B), \quad (2.2)$$

where  $\delta_D(x)$  is the Dirac delta function.  $e_i$  and  $W_{ij}$  can be written explicitly as functions of the site occupation variables  $s_i$  and  $s_j$ :

$$e_i = e_A \delta(s_i, s_A) + e_B \delta(s_i, s_B), \quad (2.3a)$$

$$W_{ij} = \sum_{\alpha=A}^B \sum_{\beta=A}^B W_{\alpha\beta} \delta(s_i, s_\alpha) \delta(s_j, s_\beta), \quad (2.3b)$$

where  $\delta(s_i, s_\alpha)$  is the Kronecker delta function and the summations indicate that  $\alpha$  and  $\beta$  take on the values  $A$  and  $B$ .

In a disordered solid it is the configurationally averaged properties that are of physical interest. The configurationally averaged Green's function is defined by the relation

$$\begin{aligned} \bar{G}_{ij}(\epsilon) = & \int \int \cdots \int \langle \psi_i | [\epsilon I - H(\{s_k\})]^{-1} | \psi_j \rangle \\ & \times p_1(s_1) p_2(s_2) \cdots p_k(s_k) \cdots \\ & \times ds_1 ds_2 \cdots ds_k \cdots \end{aligned} \quad (2.4)$$

The Hamiltonian  $H$  is defined on the Hilbert space  $\Omega$ , and  $\psi_i$  and  $\psi_j$  are the basis vectors defined in  $\Omega$  such that  $H_{ij} = \langle \psi_i | H | \psi_j \rangle$ .

Since the averaged Green's function is defined in terms of an integral over independent random variables we can use the augmented space formalism<sup>11</sup> to evaluate this integral by constructing a Hilbert space  $\Phi$ , a vector  $\gamma_0$  in  $\Phi$ , and a self-adjoint operator  $\mathcal{H}$  on the Hilbert space  $\Sigma = \Omega \otimes \Phi$  such that

$$\bar{G}_{ij}(\epsilon) = \langle \psi_i \otimes \gamma_0 | (\epsilon I_\Sigma - \mathcal{H})^{-1} | \psi_j \otimes \gamma_0 \rangle, \quad (2.5)$$

where  $I_\Sigma$  is the identity operator on  $\Sigma$  and  $\otimes$  denotes the direct or tensor product. Thus config-

urational averages in real space are replaced by inner products in the augmented space  $\Sigma$ . Intuitively, one can think of  $\Phi$  as a "disorder" space which allows for all possible configurations. The new Hamiltonian  $\mathcal{H}$  retains the physical information in its action on  $\Omega$ , and the action on  $\Phi$  builds in the appropriate probabilities for each configuration.

The key feature of the mathematical formalism is that  $\mathcal{H}$  can be constructed by means of a substitution rule. Each matrix element of  $H$  can be thought of as a function of the random variables  $\{s_k\}$ , and we can write  $H_{ij} = h_{ij}(\{s_k\})$ . If we substitute a suitably chosen self-adjoint operator  $\mathcal{S}_k$  (which acts on  $\Phi$ ) for the random variable  $s_k$ , then  $h_{ij}(\{s_k\})$  becomes an operator on  $\Phi$ , and  $\mathcal{H}$  defined by  $\mathcal{H}_{ij} = h_{ij}(\{\mathcal{S}_k\})$  is the desired operator on  $\Sigma$ . For example, if  $h_{ij}(\{s_k\}) = c$ , a (nonrandom) constant, then  $h_{ij}(\{\mathcal{S}_k\}) = cI_\Phi$ . If  $h_{ij}(\{s_k\}) = s_1 + s_2$ , then  $h_{ij}(\{\mathcal{S}_k\}) = \mathcal{S}_1 + \mathcal{S}_2$ .

We still need to describe how the disorder space  $\Phi$ , the vector  $\gamma_0$  and the operators  $\mathcal{S}_k$  are chosen. For each random variable  $s_k$ , we find a Hilbert space  $\phi_k$ , a unit vector  $v_0^k$  in  $\phi_k$ , and a self-adjoint operator  $M_k$  (on  $\phi_k$ ) such that

$$p_k(s_k) = -\frac{1}{\pi} \lim_{s \rightarrow s_k + i0^+} \text{Im} \langle v_0^k | (sI_k - M_k)^{-1} | v_0^k \rangle, \quad (2.6)$$

where  $I_k$  is the identity operator on the space  $\phi_k$ . In other words,  $v_0^k$  and  $M_k$  are chosen such that the spectral density of  $M_k$  with respect to  $v_0^k$  is the given probability distribution. Such a relation can always be found for any probability density  $p$ . For the binary alloy, with the probability distribution given in Eq. (2.2), we find that  $\phi_k$  is a Hilbert space of dimension 2,

$$\begin{aligned} M_k &= \begin{pmatrix} a & b \\ b & c \end{pmatrix}, \\ a &= s_A c_A + s_B c_B, \\ b &= (s_A - s_B) \sqrt{c_A c_B}, \\ c &= s_A + s_B - a, \end{aligned} \quad (2.7)$$

and the appropriate vector<sup>19</sup>

$$v_0^k = \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

In terms of the Hilbert space  $\phi_k$  and the operators and vectors defined on this space, we can define the essential elements needed for the transformation to the augmented space. We define

$$\Phi = \phi_1 \otimes \phi_2 \otimes \cdots \otimes \phi_k \otimes \cdots, \quad (2.8a)$$

$$\gamma_0 = v_0^1 \otimes v_0^2 \otimes \cdots \otimes v_0^k \otimes \cdots, \quad (2.8b)$$

$$\mathcal{S}_k = I_1 \otimes I_2 \otimes \cdots \otimes I_{k-1} \otimes M_k \otimes I_{k+1} \otimes \cdots. \quad (2.8c)$$

The fact that  $\mathcal{S}_k$  is equal to the identity operator on all except the  $k$ th component of  $\Phi$  is an expres-

sion of the independence of the random variables.

Using the above definition we can now apply the substitution rule to obtain the augmented space Hamiltonian  $\mathcal{H}$  for which Eq. (2.5) is valid. Substituting the direct product operator  $\mathcal{S}_i$  defined in (2.8c) into the expressions given for the diagonal and off-diagonal elements of the real-space Hamiltonian in Eq. (2.3) we have

$$\mathcal{H}_{ii} = e_A \delta(s_A I_\Phi, \mathcal{S}_i) + e_B \delta(s_B I_\Phi, \mathcal{S}_i), \quad (2.9a)$$

$$\mathcal{H}_{ij} = \sum_{\alpha=A}^B \sum_{\beta=A}^B W_{\alpha\beta} \delta(s_\alpha I_\Phi, \mathcal{S}_i) \delta(s_\beta I_\Phi, \mathcal{S}_j). \quad (2.9b)$$

In order to complete the transformation to augmented space we must define what we mean by the Kronecker delta function of the operator  $\mathcal{S}_i$ . From spectral theory we know that  $\delta(s_\alpha I_\Phi, \mathcal{S}_i)$  is the projection onto the eigenvector associated with the eigenvalue  $s_\alpha$ .<sup>20</sup> In order to find the matrix representation of the Kronecker delta, we first note that

$$\delta(s_\alpha I_\Phi, \mathcal{S}_i) = I_1 \otimes I_2 \otimes \cdots \otimes I_{i-1} \otimes \delta(s_\alpha I_i, M_i) \otimes I_{i+1} \cdots. \quad (2.10)$$

In order to calculate  $\delta(s_\alpha I_i, M_i)$  we diagonalize  $M_i$ ;

$$M_i = U \begin{pmatrix} s_A & 0 \\ 0 & s_B \end{pmatrix} U^*, \quad (2.11)$$

where

$$U = \begin{pmatrix} \sqrt{c_A} & \sqrt{c_B} \\ \sqrt{c_B} & -\sqrt{c_A} \end{pmatrix}, \quad (2.12)$$

is unitary. Thus<sup>21</sup>

$$\delta(s_\alpha I_i, M_i) = U \begin{pmatrix} \delta(s_\alpha, s_A) & 0 \\ 0 & \delta(s_\alpha, s_B) \end{pmatrix} U^*, \quad (2.13)$$

and hence

$$F_i^A \equiv \delta(s_A I_i, M_i) = \begin{pmatrix} c_A & (c_A c_B)^{1/2} \\ (c_A c_B)^{1/2} & c_B \end{pmatrix}, \quad (2.14a)$$

$$F_i^B \equiv \delta(s_B I_i, M_i) = \begin{pmatrix} c_B & -(c_A c_B)^{1/2} \\ -(c_A c_B)^{1/2} & c_A \end{pmatrix}. \quad (2.14b)$$

Substituting these expressions for the delta functions in Eq. (2.9) we find that the elements of the augmented space Hamiltonian  $\mathcal{H}$  can be written as

$$\mathcal{H}_{ii} = I_1 \otimes I_2 \otimes \cdots \otimes (e_A F_i^A + e_B F_i^B) \otimes I_{i+1} \cdots, \quad (2.15a)$$

$$\mathcal{H}_{ij} = \sum_{\alpha=A}^B \sum_{\beta=A}^B W_{\alpha\beta} (I_1 \otimes I_2 \otimes \cdots \otimes F_i^\alpha \otimes I_{i+1} \cdots \otimes F_j^\beta \otimes I_{j+1} \cdots), \quad i \neq j. \quad (2.15b)$$

Using these definitions  $\bar{G}_{ij}(\epsilon)$  can now be evaluated from Eq. (2.5).

As we mentioned earlier, Mookerjee<sup>15</sup> has also attempted to treat off-diagonal disorder using the augmented space formalism. As he noted, he failed to include the correlations between sites correctly. He simply replaced the hopping integrals randomly and thus neglected the fact that if site  $i$  contains an  $A$  atom then  $W_{ij}$  must equal  $W_{AA}$  or  $W_{AB}$  for all  $j$  coupled to  $i$ . Similarly if site  $i$  contains a  $B$  atom  $W_{ij}$  must be  $W_{BA}$  or  $W_{BB}$ . The theory we have presented in this section properly accounts for these correlations between sites.

So far we have described the augmented space formalism for determining the configurationally averaged Green's function of an alloy with off-diagonal as well as diagonal disorder. This involves choosing an appropriate set of independent random variables to describe the system, constructing the augmented space, and finding a matrix representation for the Kronecker delta function in the augmented space. Everything to this point is exact. It still remains for us to describe the computational procedures we have used for evaluating the Green's function in this formalism and some illustrative examples. In Secs. III and IV we describe two such techniques, the recursion and graphical methods, and illustrate their use for a one-dimensional alloy.

### III. RECURSION METHOD

The recursion method of Haydock, Heine, and Kelly<sup>16</sup> is a form of the Lanczos<sup>22</sup> procedure to invert matrices. The essential element of this method is an algorithm which constructs a tridiagonal representation for any operator. For the operator  $R$  defined on the Hilbert space  $\Psi$  and the vector  $|1\rangle$  in  $\Psi$  we can construct an orthonormal basis in which  $R$  is tridiagonal by the following algorithm:

$$|n+1\rangle = R|n\rangle - \alpha_n|n\rangle - \beta_{n-1}|n-1\rangle \quad \text{for } n \geq 1, \beta_0 = 0, \quad (3.1)$$

where

$$\alpha_n = \frac{\langle n|R|n\rangle}{\langle n|n\rangle}, \quad \beta_{n-1} = \frac{\langle n|n\rangle}{\langle n-1|n-1\rangle}. \quad (3.2)$$

With respect to the normalized system,  $|n\rangle / (\langle n|n\rangle)^{1/2}$ ,  $R$  is tridiagonal with diagonal elements  $R_{nn} = \alpha_n$  and off-diagonal elements  $R_{n,n+1} = R_{n+1,n} = \sqrt{\beta_n}$ .

Once we have constructed a tridiagonal representation of  $R$ , it is relatively easy to generate a continued fraction expansion for the Green's function,  $g(z) = (zI - R)^{-1}$ . Let  $D_n$  be the determin-

ant of the matrix derived from  $g(z)^{-1} = zI - R$  by deleting the first  $n$  rows and columns.  $D_0$  is the determinant of the complete matrix  $g^{-1}$ , and by the standard relation from linear algebra

$$\{1|g|1\} = D_1/D_0. \quad (3.3)$$

Expanding the determinant we obtain the recurrence relation

$$D_n = (z - \alpha_n)D_{n-1} - \beta_n D_{n-2}. \quad (3.4)$$

Substituting (3.4) into (3.3) yields the continued fraction expansion for the Green's functions,

$$\{1|g|1\} = \frac{1}{z - \alpha_1 - \frac{\beta_1}{z - \alpha_2 - \frac{\beta_2}{z - \alpha_3 \cdots}}}. \quad (3.5)$$

In the recursion method we calculate  $(\alpha_n, \beta_n)$  for  $n=1, 2, \dots, n_0$  and use a repetitive termination for the remainder of the continued fraction.

There are a number of possible termination procedures; several of these are discussed by Haydock *et al.*<sup>16</sup> Such an approximation gives the contribution of the first  $2n_0$  moments of  $R$  exactly. All higher moments are approximated in terms of these first  $2n_0$  moments.

Applying this procedure to the augmented space Hamiltonian allows one to evaluate the configurationally averaged Green's function. For example, if we wish to calculate the average density of states  $n(\epsilon)$ , which is given by the relation

$$n(\epsilon) = -\frac{1}{\pi} \lim_{z \rightarrow \epsilon + i0^+} \text{Im} \bar{G}_{ii}(z), \quad (3.6)$$

we let  $R = \mathcal{H}$  and  $|1\rangle = |\psi_i \otimes \gamma_0\rangle$  and then use the recursion relation to evaluate the diagonal element of the averaged Green's function  $\bar{G}_{ii}(z)$ .

Before discussing some example calculations, let us consider what information about the alloy is included by this approximation. The recursion method constructs new vectors  $|n+1\rangle$  in the augmented space  $\Sigma$  as a linear combination of states which are "nearest" neighbors of the states in  $|n\rangle$ . (The nearest-neighbor structure of the augmented space is discussed more fully in Sec. IV.) Therefore each level in the recursion method includes information about how the next group of neighboring states interacts with the preceding group. Since the augmented space includes information about the physical interactions as well as the configurations of the alloy, we are in a sense systematically constructing the Green's function by bringing in a growing number of atomic sites and their possible configurations. This procedure is physically reasonable and the resulting Green's function is always analytic. Many earlier attempts to extend the CPA

to include cluster correlations and off-diagonal disorder have produced nonanalytic Green's functions.<sup>23-25</sup>

While the theory we have presented is applicable to one-, two-, or three-dimensional alloys, we have chosen to calculate the density of states of a one-dimensional binary alloy since it is relatively easy to calculate exact results for one-dimensional systems. In Fig. 1 the results of a calculation using the augmented space formalism and the recursion method with  $n_0=10$  are compared with essentially exact results obtained using the Schmidt method.<sup>26</sup> The theory agrees reasonably well with exact results even for this split-band case. It correctly predicts some of the major peaks in the density of states and approximately matches the unequal band widths of the two bands. The structure predicted by the theory is naturally dependent upon  $n_0$ . In Fig. 2 we show calculations for the same one-dimensional system as in Fig. 1 but with  $n_0=7, 9$ , and 10. Notice that with increasing  $n_0$  new peaks appear in the distribution and existing ones tend to shift and narrow. For three-dimensional alloys, the exact density of states is considerably smoother<sup>27,28</sup> and fewer levels in the recursion method may be needed. An example of the application of the recursion method to a three-dimensional simple cubic solid for the special case of diagonal disorder only has already been given by Mookerjee.<sup>12</sup>

#### IV. GRAPHICAL METHOD

Another technique for evaluating the configurationally averaged Green's function in the augmented space formalism and one which may give better physical insight into the nature of this new space

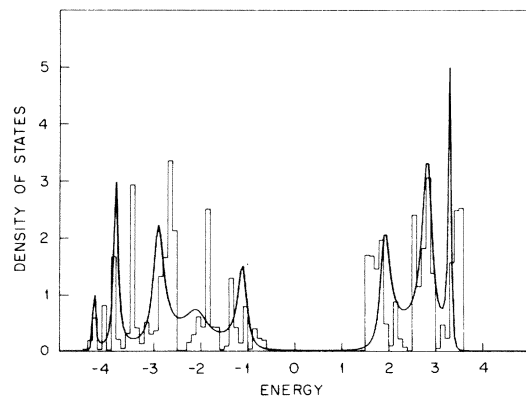


FIG. 1. The density of states calculated in the augmented space formalism by the recursion method with  $n_0=10$  is compared with exact results (histogram) for a one-dimensional electronic alloy with  $e_A = -e_B = 2.5$ ,  $W_{AA} = 0.5$ ,  $W_{AB} = W_{BA} = 0.8$ ,  $W_{BB} = 1.0$ , and  $c_B = 0.5$ .

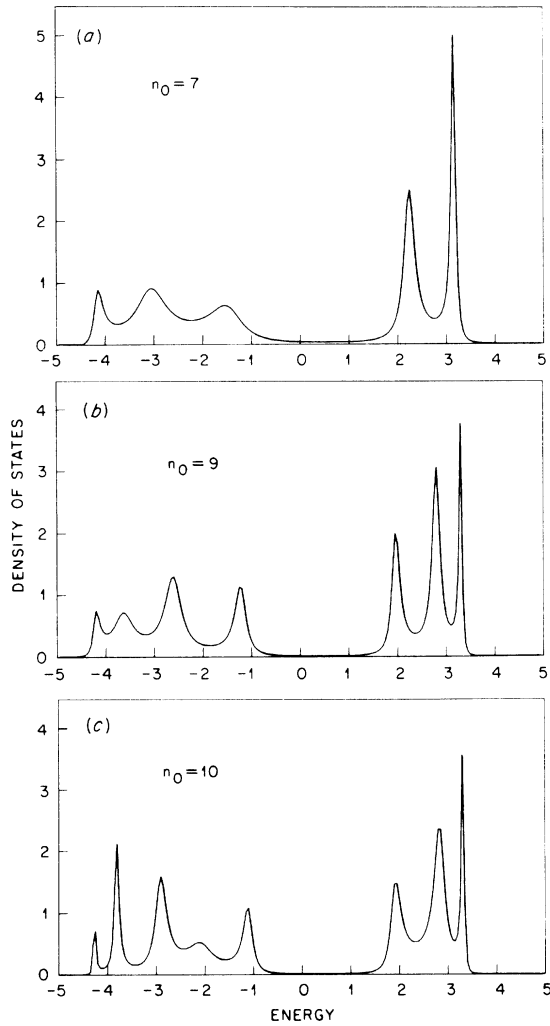


FIG. 2. The density of states for the same one-dimensional system as is used in Fig. 1 is evaluated in the augmented space formalism by the recursion method with (a)  $n_0 = 7$ , (b)  $n_0 = 9$ , and (c)  $n_0 = 10$ .

is the graphical method of Anderson.<sup>17</sup> This method was introduced by Anderson to study diffusion in random lattices and was later used by Bishop and Mookerjee<sup>13</sup> to calculate the density of states of diagonally disordered solids. In this section we apply this method to an alloy with diagonal and off-diagonal disorder.

In the graphical method, a diagonal element of the Green's function is expressed in a perturbation series in which each term corresponds to a different self-avoiding path which starts and ends at a particular site. In order to calculate the density of states in the augmented space formalism [Eq. (3.6)] we need to evaluate the inner product  $\langle \psi_i \otimes \gamma_0 | (zI_E - \mathcal{H})^{-1} | \psi_i \otimes \gamma_0 \rangle$ .

Before describing the application of the graphical

method to this problem, let us define a simpler notation for the set of vectors we use to span the augmented space  $\Sigma$ . In the description of the augmented space given in Sec. II we described the space in terms of the vectors

$$| \psi_i \otimes v_{\alpha_1}^1 \otimes v_{\alpha_2}^2 \otimes \cdots \otimes v_{\alpha_k}^k \otimes \cdots \rangle,$$

where  $i$  is the atomic site index and  $\alpha_k = 0$  or  $1$ . Following the notation of Mookerjee we set

$$\begin{aligned} |if\rangle &= | \psi_i \otimes \gamma_0 \rangle, \\ |if_j\rangle &= | \psi_i \otimes v_0^1 \otimes v_0^2 \otimes \cdots \otimes v_0^{j-1} \otimes v_1^j \otimes v_0^{j+1} \cdots \rangle, \\ |if_j v\rangle &= | \psi_i \otimes v_0^1 \otimes \cdots \otimes v_0^{j-1} \otimes v_1^j \otimes v_0^{j+1} \cdots \otimes v_0^{i-1} \\ &\quad \otimes v_1^i \otimes v_0^{i+1} \cdots \rangle, \text{ etc.} \end{aligned} \quad (4.1)$$

where  $v_1^k$  is the vector in  $\phi_k$  orthonormal to  $v_0^k$  and  $v_1^k = \binom{0}{1}$  for the representation of  $M_k$  given in Eq. (2.7). The index  $i$  is referred to as the site index and  $f, j, \dots$  as the field indices.

We separate the augmented space Hamiltonian into a diagonal part and an off-diagonal part,

$$\mathcal{H} = \mathcal{H}^d + \mathcal{H}^o. \quad (4.2)$$

Note that this division of  $\mathcal{H}$  is not equivalent to that given in Eq. (2.15) since  $\mathcal{H}^d$  is diagonal in the field indices as well as the site index. Then according to Anderson we can write the diagonal element of the averaged Green's function as

$$\begin{aligned} \bar{G}_{00}(z) &= \langle 0f | (zI_E - \mathcal{H})^{-1} | 0f \rangle \\ &= \left( g_{0f}^{-1} - \sum_{k \neq 0f} \mathcal{H}_{0f, k}^o G_k^{of} \mathcal{H}_{k, 0f}^o \right. \\ &\quad \left. - \sum_{\substack{k \neq 0f \\ l \neq k, 0f}} \mathcal{H}_{0f, l}^o G_l^{of, k} \mathcal{H}_{l, k}^o G_k^{of} \mathcal{H}_{k, 0f}^o \cdots \right)^{-1}, \end{aligned} \quad (4.3)$$

where

$$g_k = \langle k | (zI_E - \mathcal{H}^d)^{-1} | k \rangle, \quad (4.4)$$

$$\begin{aligned} G_k^{of} &= \left( g_k^{-1} - \sum_{l \neq k, 0f} \mathcal{H}_{k, l}^o G_l^{of, k} \mathcal{H}_{l, k}^o \right. \\ &\quad \left. - \sum_{\substack{l \neq k, 0f \\ m \neq l, k, 0f}} \mathcal{H}_{k, m}^o G_m^{of, k, l} \mathcal{H}_{m, l}^o G_l^{of, k} \mathcal{H}_{l, k}^o \cdots \right)^{-1}. \end{aligned} \quad (4.5)$$

$G_k^{of, k}$ ,  $G_k^{of, k, l}$ , etc. are defined by similar expressions.

The graphical method of Anderson eliminates repeated indices in each term of the perturbation expansion of  $\bar{G}_{00}$  by defining renormalized Green's functions  $G_i^{i, j, \dots}$  which are expressed in terms of summations which do not include the vectors  $i, j, \dots$ . If we draw a line connecting the points in the sequence in which they appear in each term of

the expansion we find that the expansion for  $\bar{G}_{00}$  can be expressed as a collection of closed self-avoiding paths in the augmented space. In addition each renormalized Green's function can be expressed in terms of a restricted subset of those closed paths defining  $\bar{G}_{00}$ .

It is best to begin with the simpler problem of a solid with only diagonal disorder which was treated by Bishop and Mookerjee.<sup>13</sup> By setting  $W = W_{AA} = W_{AB} = W_{BA} = W_{BB}$ , we can reduce the augmented space Hamiltonian given in Eq. (2.15) to

$$\mathcal{H}_{i,j} = W(I_1 \otimes I_2 \cdots \otimes I_k \cdots) \quad (4.6)$$

with  $\mathcal{H}_{i,i}$  unchanged. This is equivalent to the form of the augmented space Hamiltonian given by Bishop and Mookerjee in Eq. (8) of Ref. 13. In approximating the diagonal element of the Green's function for this simplified Hamiltonian, Bishop and Mookerjee included all closed self-avoiding loops except those which connected different spatial sites through vectors with changes in the field indices. This approximation turned out to be exactly equivalent to the coherent-potential approximation (CPA) of Soven<sup>1</sup> and Taylor.<sup>2</sup>

When considering the full augmented space Hamiltonian which includes off-diagonal and diagonal disorder such an approximation is inadequate. It is the paths which have different spatial sites connected by way of vectors with changes in the field indices which account for the particular structural correlations. Since each off-diagonal element is a function of the occupancy of the two neighboring sites, we must at least include loops which have pairs of neighboring sites connected by way of vectors with changes in the field indices associated with that pair of sites. Therefore for an adequate approximation for the off-diagonal disordered alloy, we need to include two sets of closed self-avoiding paths: (i) We need all the paths which do not allow different spatial sites to be connected through changes in the field indices. (In fact, the collection of all paths with only spatial index changes corresponds to the virtual crystal approximation.<sup>29</sup>) (ii) In addition, we need a subset of the remaining closed self-avoiding loops which allow for the configuration dependence of nearest-neighbor sites as discussed above.

This concept can best be illustrated by example. We again choose to examine a one-dimensional binary alloy with nearest-neighbor hopping as we did in Sec. III. We label the real-space lattice structure relative to a central site 0 as  $(\cdots -2, -1, 0, 1, 2 \cdots)$ . Figure 3 shows a graph of  $|0f\rangle$  and its nearest neighbors in augmented space. The lines indicate the matrix elements between vectors. (For diagonal disorder only, there are just 3 nearest neighbors,  $0f, 1f, -1f$ , instead of 9.) Since there

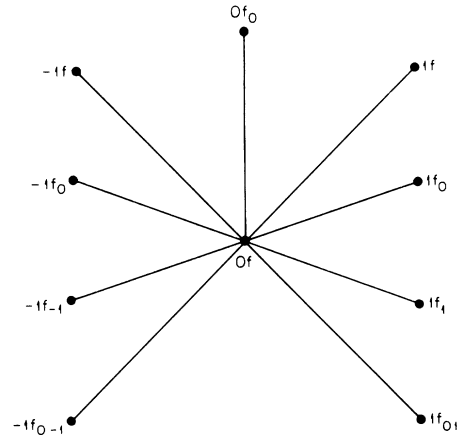


FIG. 3. The augmented space graph of the nearest neighbors of vector  $|0f\rangle$  for the one-dimensional alloy with both diagonal and off-diagonal disorder.

are no closed loops connecting different spatial sites through changes in field indices this graph is inadequate to use for developing an approximation for  $\bar{G}_{00}$ . If we include second nearest neighbors as is shown in Fig. 4, we get a considerably more complex structure with many self-avoiding closed loops starting at  $0f$  and returning via a path of the desired structure. The simplest set of closed self-avoiding paths satisfying our requirements for having different spatial sites connected by changes in field indices is the collection of 12 third-order loops starting and ending at  $0f$ . These include the paths with the following pairs of intermediate vectors:  $(0f_0, 1f), (0f_0, 1f_1), (0f_0, 1f_0), (0f_0, 1f_{0,1}), (0f_0, -1f), (0f_0, -1f_{-1}), (0f_0, -1f_0), (0f_0, -1f_{0,-1}), (1f, 1f_1), (1f_0, 1f_{0,1}), (-1f, -1f_{-1}), (-1f_0, 1f_{0,-1})$ . For diagonal disorder only, the shortest path in augmented space satisfying the requirements of different atomic sites connected through changes in field indices is eight steps long instead of the three

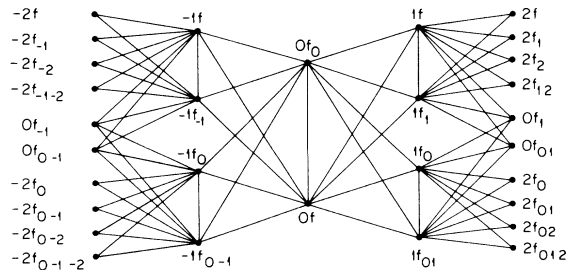


FIG. 4. The augmented space graph of the first and second nearest neighbors of vector  $|0f\rangle$  for the one-dimensional alloy with both diagonal and off-diagonal disorder.

steps as it is for the off-diagonal disorder case. This reduction in the length of the closed loops which results from including off-diagonal disorder is a clear indication of the increase in importance of correlations between different sites in this system. In a one-dimensional structure all paths not involving different spatial sites connected by changes in field indices correspond to hops to a nearest-neighbor vector and back.

If we write the equations for  $\bar{G}_{00}$  for the set of paths described above, we find it is a function of the 9 independent renormalized Green's functions:  $G_{0f_0}^{0f}$ ,  $G_{1f}^{0f}$ ,  $G_{1f_0}^{0f}$ ,  $G_{1f_1}^{0f}$ ,  $G_{1f_{01}}^{0f}$ ,  $G_{1f^{*0}f_0}^{0f}$ ,  $G_{1f_1^{*0}f_0}^{0f}$ ,  $G_{1f_1^{*1}f}^{0f}$ ,  $G_{1f_{01}^{*1}f_0}^{0f}$ . In order to evaluate each of these renormalized Green's functions, we write the equations for the same set of paths as we used for  $\bar{G}_{00}$  except with those matrix elements set to zero which correspond to the particular set of restrictions on each renormalized Green's function. This procedure generates a self-consistent set of equations for  $\bar{G}_{00}$  which can be easily solved numerically. (A more detailed description of the approximation is contained in the Appendix.)

The density of states evaluated by the graphical method is compared with essentially exact results for a one-dimensional binary alloy with  $e_A = -e_B = 2.5$ ,  $W_{AA} = 0.5$ ,  $W_{AB} = W_{BA} = 0.8$ ,  $W_{BB} = 1$ , and  $c_A = 0.1, 0.3$ , and  $0.5$  in Figs. 5(a), 5(b), and 5(c), respectively. The theory predicts a relatively smooth two-band structure which adequately reproduces the average properties of the exact density of states but which does not reproduce the detailed structure. This result is similar in form to the CPA results for diagonally disordered systems. The essential difference lies in the fact that we are able to reproduce the unequal bandwidths which are associated with off-diagonal disorder.

The solution we have presented above is for the simplest set of closed self-avoiding paths which are adequate to approximate a disordered linear chain with off-diagonal disorder. In order to improve the approximation, more closed self-avoiding paths must be included. By choosing those paths which connect vectors associated with particular groupings of atoms one can include whatever structure is desired in the density of states.

The graphical method is not restricted to the one-dimensional examples described above. Mookerjee<sup>14</sup> has used it successfully to solve for the density of states of a diagonally disordered three-dimensional diamond lattice. Furthermore, Bishop and Mookerjee<sup>13</sup> have shown that the form of the Green's function generated by the graphical method is always analytic. As we indicated already in Sec. III, this is an important property which was not found in many earlier theories.

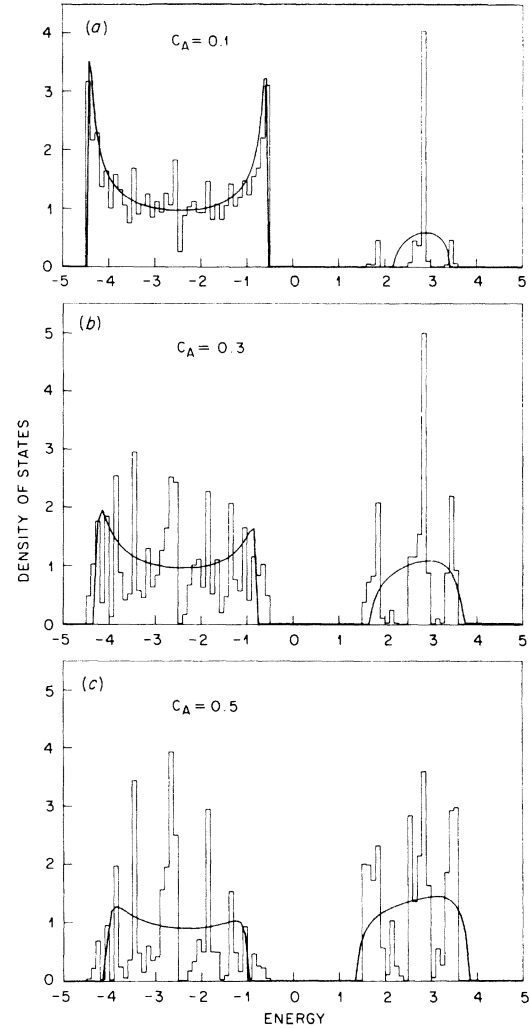


FIG. 5. The density of states evaluated by the graphical method is compared with exact results (histogram) for one-dimensional electronic alloys with  $e_A = -e_B = 2.5$ ,  $W_{AA} = 0.5$ ,  $W_{AB} = W_{BA} = 0.8$ ,  $W_{BB} = 1.0$ , and (a)  $c_A = 0.1$ , (b)  $c_A = 0.3$ , and (c)  $c_A = 0.5$ .

## V. CONCLUSION

We have presented a formalism for constructing a nonrandom representation of a random substitutional alloy with both diagonal and off-diagonal disorder and have described two separate computational methods for approximating the Green's function of this system. The theory is based on Mookerjee's method for averaging functions of independent random variables and parallels his development for the special case of diagonal disorder only. We believe the recursion method and the graphical method are only two of many possible techniques for approximating the Green's function.<sup>18</sup> It is the transformation to augmented space which is the

essential feature of this theory. Once the augmented space is constructed then it should not be difficult to devise a satisfactory approximation for evaluating the configurationally averaged property of interest.<sup>30, 31</sup>

While the theory we have presented includes off-diagonal as well as diagonal disorder and includes multisite correlations in a random system, it cannot be considered a general theory for disordered solids. In order to be considered a general theory it would have to be able to include short-range order; i.e., systems which are described in terms of functions of nonindependent random variables. The theory as presented is based on the assumption of independence of the random variables. A generalization of the augmented space formalism not based on independent random variables which is applicable to disordered systems with short-range order will be dealt with in a subsequent paper.

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#### APPENDIX

There are 12 third-order self-avoiding paths starting and ending at site  $0f$  in Fig. 4. The 12 pairs of intermediate sites on these paths are  $(0f_0, 1f)$ ,  $(0f_0, 1f_1)$ ,  $(0f_0, 1f_0)$ ,  $(0f_0, 1f_{01})$ ,  $(0f_0, -1f)$ ,  $(0f_0, -1f_{-1})$ ,  $(0f_0, -1f_0)$ ,  $(0f_0, -1f_{0-1})$ ,  $(1f, 1f_1)$ ,  $(1f_0, 1f_{01})$ ,  $(-1f, -1f_{-1})$ ,  $(-1f_0, -1f_{0-1})$ . If we apply Anderson's perturbation expansion given in Eq. (4.3) and include the fact that contributions from paths including negative sites are equivalent to ones including positive sites [i.e., the contribution from  $(0f_0, 1f)$  equals that from  $(0f_{01}, -1f)$ ], then

$$\begin{aligned} \bar{G}_{00}(z) = & [z - a - b^2\hat{G}_1 - 2A^2\hat{G}_2 - 2B^2(\hat{G}_3 + \hat{G}_4) - 2D^2\hat{G}_5 \\ & - 4b\hat{G}_1(B\hat{G}_6A - D\hat{G}_7B - E\hat{G}_6B - F\hat{G}_7D) \\ & - 4A\hat{G}_2b\hat{G}_8B - 4B\hat{G}_3b\hat{G}_9D]^{-1}, \end{aligned} \quad (A1)$$

where  $a$  and  $b$  are defined in Eq. (2.7),

$$\begin{aligned} m(0f, 1f) &= A = c_A^2 W_{AA} + 2c_A c_B W_{AB} + c_B^2 W_{BB}, \\ m(0f, 1f_0) &= B = (c_A c_B)^{1/2} [c_A W_{AA} + (c_B - c_A) W_{AB} \\ & \quad - c_B W_{BB}] \\ m(0f, 1f_{01}) &= D = c_A c_B (W_{AA} - 2W_{AB} + W_{BB}) \\ m(0f_0, 1f_0) &= E = c_A c_B W_{AA} + (c_A^2 + c_B^2) W_{AB} + c_{AB} W_{BB} \\ m(0f_0, 1f_{01}) &= F = (c_A c_B)^{1/2} [c_B W_{AA} + (c_A - c_B) W_{AB} \\ & \quad - c_A W_{BB}] \end{aligned} \quad (A2)$$

and  $\hat{G}_1 = G_{0f_0, 0f}^{0f}$ ,  $\hat{G}_2 = G_{1f, 0f}^{0f}$ ,  $\hat{G}_3 = G_{1f_0, 0f}^{0f}$ ,  $\hat{G}_4 = G_{1f_1, 0f}^{0f}$ ,  $\hat{G}_5 = G_{1f_{01}, 0f}^{0f}$ ,  $\hat{G}_6 = G_{1f, 0f_0}^{0f}$ ,  $\hat{G}_7 = G_{1f_1, 0f_0}^{0f}$ ,  $\hat{G}_8 = G_{1f_1, 1f}^{0f}$ ,  $\hat{G}_9 = G_{1f_{01}, 1f_0}^{0f}$ .  $m(i, j)$  is the matrix element connecting vectors  $i$  and  $j$ . Note that each loop must be counted twice since you can traverse it in either direction.

In order to evaluate the renormalized Green's functions we use Eq. (4.5) and the same set of paths as we used for  $\bar{G}_{00}$  with the appropriate restrictions included. For example,  $G_{0f_0}^{0f}$  is evaluated by setting the matrix element connecting  $0f$  and  $0f_0$  to zero (leaving only 4 third-order loops) in order to eliminate the paths that correspond to hops from  $0f_0$  to  $0f$ . We find

$$\begin{aligned} G_{0f_0}^{0f} = \hat{G}_1 = & (z + a - 2A^2\hat{G}_2 - 2B^2\hat{G}_3 - 2B^2\hat{G}_4 - 2D^2\hat{G}_5 \\ & - 4A\hat{G}_2b\hat{G}_8 - 4B\hat{G}_3b\hat{G}_4)^{-1}. \end{aligned} \quad (A3)$$

Similarly we find for the remaining renormalized Green's functions,

$$\begin{aligned} \hat{G}_2 &= (\bar{G}_{00}^{-1} + A^2\hat{G}_2 + 2A\hat{G}_2b\hat{G}_8B + 2b\hat{G}_1B\hat{G}_6A)^{-1}, \\ \hat{G}_3 &= (\bar{G}_{00}^{-1} + B^2\hat{G}_4 + 2A\hat{G}_2b\hat{G}_8B + 2b\hat{G}_1B\hat{G}_6A)^{-1}, \\ \hat{G}_4 &= (\bar{G}_{00}^{-1} + 2a + B^2\hat{G}_3 + 2B\hat{G}_3b\hat{G}_9D + 2b\hat{G}_1E\hat{G}_6B)^{-1}, \\ \hat{G}_5 &= (\bar{G}_{00}^{-1} + 2a + D^2\hat{G}_5 + 2B\hat{G}_3b\hat{G}_9D + 2b\hat{G}_1F\hat{G}_7D)^{-1}, \\ \hat{G}_6 &= (\hat{G}_2^{-1} + \hat{G}_3^{-1} - 2A\hat{G}_2b\hat{G}_8B - \bar{G}_{00}^{-1})^{-1}, \\ \hat{G}_7 &= (\hat{G}_4^{-1} + \hat{G}_5^{-1} - 2a - 2B\hat{G}_3b\hat{G}_9D - \bar{G}_{00}^{-1})^{-1}, \\ \hat{G}_8 &= (\hat{G}_1^{-1} + 2B\hat{G}_3b\hat{G}_9D + B^2\hat{G}_3)^{-1}, \\ \hat{G}_9 &= (\hat{G}_1^{-1} + 2B\hat{G}_3b\hat{G}_9D + D^2\hat{G}_5)^{-1}. \end{aligned} \quad (A4)$$

These equations can be solved in less than 0.1 sec for each value of  $z$  on the ORNL 360/91.

We have included the complete set of equations in order to demonstrate the mathematical procedure. In general, it is simpler to use the computer to both generate and solve the equations.

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