PHYSICAL REVIEW B VOLUME 13, NUMBER 10 15 MAY 1976

New approach to the study of binary alloys

Pabitra N. Sen
Xerox Palo Alto Research Center, Palo Alto, California 94304

Felix Yndurain*
Department of Physics,† University of California, Berkeley, California 94720

(Received 4 August 1975)

We have developed a method to study the electronic densities of states in disordered binary alloys where correlation and clustering effects can be large. In this method, we consider a large cluster of atoms surrounded by a Bethe lattice. Any strong clustering and correlation effects can be built into the cluster. Assuming a mean-field approximation in the Bethe lattice, we can treat the cluster exactly by solving a set of linear equations. In the present work we have studied the coherent-potential approximation and the Bethe-Peierls approximation for the mean-field Bethe lattice. Then we have studied the systematics of densities of states at a central site of various different clusters consisting of different numbers of atoms ranging from 5 to 29 and of various compositions. An averaged density of states per site has been calculated for a linear chain and compared with numerical and other calculations. We have outlined a procedure for obtaining an estimate of the optimum cluster sizes based on localization of wave functions. The present method is simple, fast, and free from any undesirable singularity in the self-energy which has marred all the previous attempts to go beyond single-site coherent-potential approximation.

I. INTRODUCTION

In the last few years there has been an increasing interest in the study of the local environment effects on the electronic, vibrational, and magnetic properties of alloys.[1-5] Most of the work done has been based on the study of the single-site coherent-potential approximation (CPA)[6,7] and other effective-field approximations.[1,2]

In this work we present a new method to study the electronic properties of an alloy taking into account explicitly and exactly the local environment effects. The method is based on the cluster–Bethe-lattice method.[8,9] The main idea behind this method is to treat a cluster of atoms exactly and replace the rest of the system by a proper Bethe lattice. Then, the local environment around a particular atom in which we are interested is taken into account exactly and the rest of the system is approximated by some effective medium. This then avoids all the singularity problems that so far have marred any attempt to develop a usable self-consistent method which goes beyond simple single-site CPA. Bethe lattice avoids any spurious periodicity that might be introduced by other methods which employ cyclic boundary conditions on clusters. In this way we can study (i) the average density of states of an alloy where the local and correlation effects are significant and thus go beyond CPA or any other mean-field approximation; (ii) the effect of a given cluster of atoms in an otherwise homogeneous alloy (as an extension of the Koster-Slater problem of a single impurity in a perfect crystal) or a topologically disordered elemental system. Finally, we remark that this is the first attempt to study the effect of cellular or compositional disorder in a topologically disordered system. We never refer to a k vector which appears in other variants of any attempt to extend CPA.

Let us consider a binary alloy, whose constituents are atoms of class A and class B with concentrations X and Y, respectively $X+Y=1$. We assume that we deal with the following tight-binding Hamiltonian:

$$H=\sum_n |n\rangle\epsilon_n\langle n| + \sum_{n\neq m}|n\rangle V_{nm}\langle m| = D+W\,, \qquad (1.1)$$

where $|n\rangle$ is the single atomic orbital associate with site n. ϵ_n are the atomic levels which take the values ϵ_A and ϵ_B depending on whether an atom A or B occupies the site n. V_{nm} is the hopping integral between site n and m; we assume that V_{nm} is restricted to the nearest neighbors and is independent of the sites n and m $(V_{nm}\equiv V)$, i.e., we study the diagonal disorder only. We take the origin of energies such that $\epsilon_A=-\epsilon_B$ and we define

$$\epsilon_A=-\epsilon_B=\delta/2V\,. \qquad (1.2)$$

We can easily generalize our cluster Bethe method for the cases where there is more than one band or there is disorder in the hopping matrix. The remainder of this paper is organized as follows: In Sec. II we study cellular disorder by different mean-field approximations in a Bethe lattice. The CPA can be solved easily in the Bethe lattice giving a rather smooth and featureless density of states. The density of states in the Bethe lattice and within the Bethe-Peierls approximation[1,2] (BPA) is also studied. In Sec. III we apply the cluster–Bethe-lattice method employing the CPA in the Bethe lattice. We study the density of states of clusters of different sizes (5, 17, and 29 atoms, respectively) and different arrangement of atoms of class A and B. We analyze the results that show the importance of the local configuration in determining the density of states. In Sec. IV we study the localization of the states; we have not developed a criterium for localization but, instead, we have studied the degree of localization in a very simple and natural way. Finally, in Sec. V some concluding remarks are made.

II. MEAN-FIELD APPROXIMATIONS IN THE BETHE LATTICE

As we have stated in Sec. I the main idea of the cluster–Bethe-lattice method is to take a cluster of atoms and surround it with some effective medium that takes account of the rest of the infinite system. In our case a Bethe lattice whose sites are randomly occupied by the constituents of the alloy plays the required role of a boundary condition. Since we need to consider this boundary in an approximate way we will apply different mean-field approximations to study the Bethe lattice; (a) the single-site coherent-potential approximation (CPA)[6,7] and (b) the single-site Bethe-Peierls approximation (BPA).[1,2] The similar problem has been studied by using an improved virtual-crystal approximation.[10]

A. Coherent-potential approximation

The CPA considers only the random uncorrelated fluctuations of the site atomic energy levels which depend only on the chemical nature of the atom occupying that site. In this way all the electronic properties of an alloy depend only on the concentration of the alloy constituents.

Let G denote the full Green's function for the Bethe lattice of coordination number Z, then

$$G=(E-H)^{-1}=(E-D-W)^{-1}; \quad E=E+i0^{+}, \tag{2.1}$$

where H is the Hamiltonian [Eq. (1.1)]. Let us denote the average Green's function by $\bar{G}$. This will be the CPA Green's function, i.e., the Green's function where the orbital energy at each site of the Bethe lattice has been replaced by a self-energy $\Sigma(E)$;

$$\bar{G}=(E-W-\Sigma)^{-1}. \tag{2.2}$$

Now we can adopt the transfer matrix technique[9] to solve for the matrix elements of the Green's function $\bar{G}$ between the atom orbitals in the Bethe lattice.

Let us denote a reference site in the Bethe lattice by the index 0, its Z neighbors, being all equivalent, by an index 1, neighbors of 1 and second-nearest neighbor of 0 by 2 and so forth. Then, from Eq. (2.2) and following a standard technique[9] we get

$$\begin{aligned}
&(E-\Sigma)\bar{G}_{00}=1+ZV\bar{G}_{10},\\
&(E-\Sigma)\bar{G}_{10}=V\bar{G}_{00}+(Z-1)V\bar{G}_{20}; \qquad (2.3)\\
&(E-\Sigma)\bar{G}_{n0}=V\bar{G}_{n0}=V\bar{G}_{n-1,0}+(Z-1)VG_{n+1,0},
\end{aligned}$$

where $\bar{G}_{n,0}$ stands for the matrix element of the Green's function $\bar{G}$ between the atomic orbital in atom n and the atomic orbital in atom 0. We define the transfer matrix T (transfer function in this case) by

$$T=\bar{G}_{n+1,0}/\bar{G}_{n0}. \tag{2.4}$$

Inserting this in the repeating part of Eq. (2.3) we get[9]

$$T=\{E-\Sigma\pm[(E-\Sigma)^2-4(Z-1)V^2]^{1/2}\}/2V(Z-1) \tag{2.5}$$

then the diagonal matrix element of the Green's function at site 0 is given by

$$\bar{G}_{00}=(E-\Sigma-ZVT)^{-1}. \tag{2.6}$$

If we now assume that the site 0 is occupied by an atom of class A and the rest of the sites have the CPA self-energy $\Sigma(E)$ we get

$$\bar{G}_{00}^{A}=(E-\epsilon_A-ZVT)^{-1}. \tag{2.7a}$$

On the other hand, if the site 0 is occupied by an atom of class B we get

$$\bar{G}_{00}^{B}=(E-\epsilon_B-ZVT)^{-1}. \tag{2.7b}$$

The CPA self-consistency[6,7] requires that

$$X\bar{G}_{00}^{A}+Y\bar{G}_{00}^{B}=\bar{G}_{00}. \tag{2.8}$$

It is easy to prove that Eq. (2.8) implies that

$$X(\epsilon_A-\Sigma)[1-(\epsilon_A-\Sigma)\bar{G}_{00}]^{-1} + Y(\epsilon_B-\Sigma)[1-(\epsilon_B-\Sigma)\bar{G}_{00}]^{-1}=0. \tag{2.9}$$

This means that the average single-site scattering t matrix vanishes, which is another way to put the CPA self-consistency requirement. Equations (2.6) and (2.9) give a cubic equation on Σ that can be solved immediately.

Insertion of Σ in Eqs. (2.5) and (2.6) gives $\bar{G}_{00}$ and from it the local density of states at the site 0 is given by

$$\rho(E) = -(1/\pi)\,\mathrm{Im}\bar{G}_{00}(E + i0)\,. \qquad (2.10)$$

We have calculated the local density of states of one atom of the Bethe lattice for different Hamiltonian parameters and different concentrations. The results are shown in Fig. 1. In Fig. 1(a) we calculate the density of states for a fixed concentration and different Hamiltonian parameters, and we see how the split-band limit[7] appears for values of δ larger than a critical value. In Fig. 1(b) we have plotted the density of states for the same Hamiltonian parameters but for different concentrations. The systematics, as a function of x and δ, of the density of states closely resemble those studied in Ref. 7 and we need not elaborate on this.

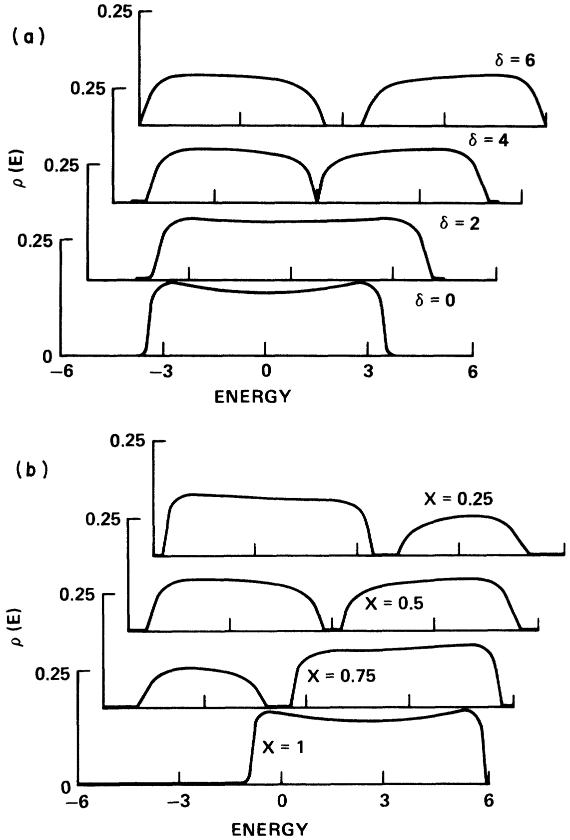

FIG. 1. (a) CPA densities of states, $\rho(E)$ for a fourfold-coordinated Bethe lattice as a function of energy E, for fixed $x = 0.5$ and various $\delta = \epsilon_A - \epsilon_B$. (b) CPA densities of states $\rho(E)$ for a fixed $\delta = 5$ and various x, the concentration of the A component.

B. Bethe-Peierls approximation

The single-site Bethe-Peierls approximation (BPA) has been developed by Brouers *et al.*[1,2] with the purpose of including the local environment effects absent in the CPA. We first derive the equation determining the self-consistent BPA self-energy $\sigma(E)$ for the Bethe lattice. The derivation is analogous to the derivation described above for the CPA. In the BPA one considers the first-nearest neighbor of an atom to be given with a desired conditional probability distribution and from the next neighbor onwards all the sites are replaced by the self-energy σ. The equation that determines $\sigma(E)$ is again the condition that the average diagonal matrix element of the Green's function at the central atom $\bar{G}_{00}$ is the same as that obtained by replacing *all* the atoms by the self-energy σ. Then we get

$$\bar{G}_{00} = \sum_{k,k'=A}^{B} \left(\sum_{I=0}^{Z} \frac{P_k(I)}{E - \epsilon_k - I V^2/[E - \epsilon_k - V(Z-1)T'] - (Z-I)V^2/[E - \epsilon_{k'} - V(Z-1)T']} \right)$$
$$= \frac{1}{E - \sigma - ZVT'} \quad (k \neq k')\,, \qquad (2.11)$$

where the transfer matrix T is now given by

$$T' = \frac{(E-\sigma) \pm [(E-\sigma)^2 - 4(Z-1)V^2]^{1/2}}{2(Z-1)V}\,. \qquad (2.12)$$

$P_A(I)$ $[P_B(I)]$ in Eq. (2.11) denotes the conditional probability that one atom of class $A(B)$ has I nearest-neighbor atoms at class $A(B)$ and $(Z-1)$ atoms of class $B(A)$.

Even though BPA appears to be quite attractive, Eq. (2.11) forms an eleventh-order equation for σ. Although the solution of an eleventh-order polynomial is straightforward, the choice of the right solution does not seem unique. We have solved for $\sigma(E)$ iteratively starting from CPA self-energy $\Sigma(E)$ as suggested by Brouers *et al.*[1] The convergence is usually rather poor except for cases where there is little difference between the CPA and BPA solutions, i.e., where the correlation between the atoms is small and are very similar for A and B (see Fig. 2). The two upper curves in Fig. 2 correspond to a random alloy with $P(I)$'s given by the binomial distribution. The BPA density of states in the bottom of Fig. 2 corresponds to a correlated alloy, where there is a slight tendency of phase separation. The values of $P(I)$'s chosen were as follows:

$$P_A(0) = P_A(1) = P_B(0) = P_B(1) = 0\,,$$

$$P_A(2) = P_A(3) = P_B(2) = P_B(3) = 0.15\,,$$

and

$$P_A(4) = P_B(4) = 0.2\,.$$

In conclusion, since the mean field in the Bethe lattice serves as a boundary condition we choose the CPA instead of the BPA for the following reasons. The CPA gives a smooth and featureless density of states, whereas the BPA does not. (See Figs. 1 and 2). The solution of CPA in the Bethe lattice is unambiguous, whereas the solution of BPA is not. The CPA gives a "neutral" background to the density of states that helps to understand better the local configuration effects on the density of states. Any other boundary condition which is more complicated than CPA are known to be plagued by singularities and branch points in Σ (related to the multiple root problem stated above).[11] Our method can precisely avoid these disagreeable troubles and is potentially superior for practical applications.

III. CLUSTER–BETHE-LATTICE METHOD

A. Three-dimensional system

Once we know how to solve for the (CPA) in the Bethe lattice we can apply the cluster–Bethe-lattice method[8,9] in order to calculate the density of states for a particular atom in the alloy. In the cluster–Bethe-lattice method a cluster of atoms is treated exactly and the rest of the system is simulated by the Bethe lattice. The local configuration is properly included in the cluster calculation. The details of the method can be found elsewhere.[9]

We have studied clusters of different sizes in order to see how important the local configuration is in determining the density of states. Here we will restrict ourselves to the study of a fourfold-coordinated topologically disordered system and study a few representative clusters. These clusters can be taken to represent a portion of a continuous random network.[8] In the rest of this work for illustrative purposes, we assume that we deal with clusters in which the atoms are topologically arrayed in a diamond lattice structure (the method can be applied to any structure[8]) so as we keep the fourfold coordinates throughout. In addition, for the Hamiltonian parameters we take $V=1$ and $\delta=5V$. All energies are now measured in units of V.

The simplest clusters we have studied are clusters of five atoms, i.e., the central, or reference atom, and its four nearest neighbors. Assuming the central atom to be of class, say, A we have studied the five possible clusters (A-$BBBB$, A-$BBBA$, A-$BBAA$, A-$BAAA$, and A-$AAAA$) surrounded by a CPA Bethe lattice with $X=0.5$ and $\delta=5$. In Fig. 3 we have shown the corresponding local densities of states. In the cluster A-$BBBB$ we get a large peak that corresponds to an almost isolated state in the A atom, on the other hand, in

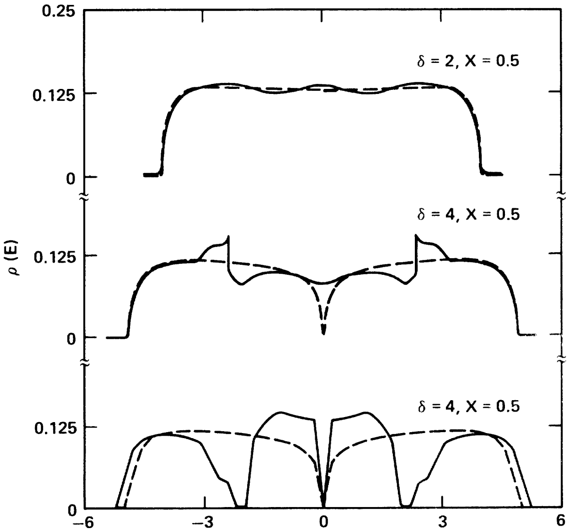

FIG. 2. Densities of states $\rho(E)$ for a Bethe lattice as a function of energy. Dashed curves stand for CPA and the solid curve for BPA. BPA cases reported here are for completely uncorrelated distribution (upper two curves) and the case where there is a slight tendency of phase separation (lowest curve). (See text.)

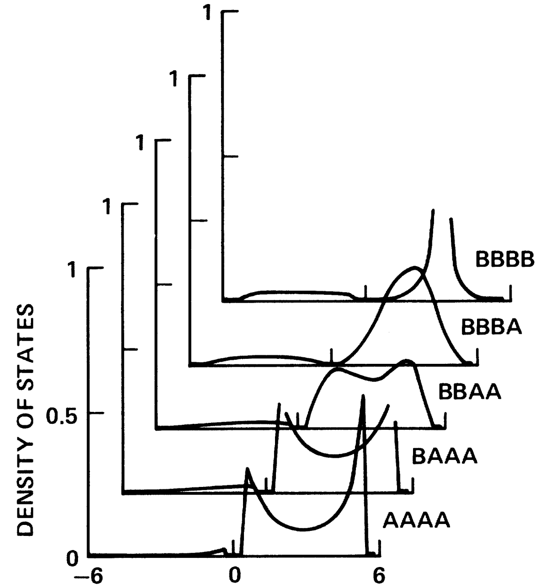

FIG. 3. Local density of states for a central A atom in a cluster of five atoms. $AAAA$ denotes a cluster where the central atom is surrounded by four A atoms; $BAAA$ denotes that with three A and one B and so forth. Bethe lattice beyond the cluster is fourfold coordinated with CPA parameters $x=0.5$ and $\delta=5$.

cluster A-$AAAA$ we get two well separated peaks that correspond to the bonding and antibonding states of the A-A pair. The smooth part of the density of states derives a parentage from B-type atoms. For the intermediate cases, the density of states is intermediate between these two extreme cases. It is interesting to note that these results do not agree with the calculations performed by Brouers *et al.*[2] using BPA; they obtain a peak in the density of states at the same value of the energy irrespective of the cluster, whereas in our calculation the position of the peaks in the density of states is very sensitive to the local configuration around the center atom (see Fig. 3). We have obtained the same results using a completely different boundary condition,[10] and in addition our results agree with Aoi's[4] calculations.

Let us now increase the size of the cluster. We take a cluster of 29 atoms such that its sites are arranged in a diamond lattice topology (see Fig. 4), we study also a cluster of 17 atoms that can be obtained from the 29-atom cluster by removing all the atoms labeled from 17 to 28 in the cluster of Fig. 4. Note that the cluster of 29 atoms includes 12 sixfold rings of bonds, whereas the cluster of 17 atoms contains none.

We have taken three different clusters such that the portion of the atoms of class A and B is random in the cluster of Fig. 4, keeping the central atom always of class A. The actual position of the atoms in the clusters is given in Table I, we see that the central atom of cluster J has three nearest neighbors of class A and one of class B; the central atom of cluster F has two nearest neighbors of class A and two of class B and finally the central atom of cluster E has one nearest neighbor of class A and three nearest neighbors of class B. We have calculated the local density of states at central or reference atom for the three 17-atom clusters and the three 29-atom clusters. The boundary condition again is a Bethe lattice of coordination four within the CPA. The recipe to get the concentration in the Bethe lattice is given by the fact that we assume that the cluster we take is representative of the alloy, then the concentration in the cluster and in the Bethe lattice is the same. In the clusters of 17 and 29 atoms we have analyzed the concentration to be $x = y = 0.5$.

In Figs. 5–7 we have drawn the local density of states calculated for the clusters J, F, and E,

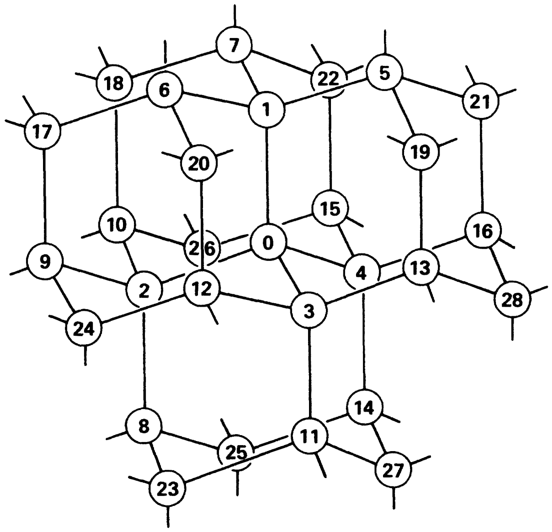

FIG. 4. Cluster of 29 atoms. Short line from an atom denotes a bond that connects it to a Bethe lattice. Occupancy of various sites numbered 0–28 are given in Table I for the clusters considered in this paper.

TABLE I. Configurations of clusters E, F, and J. Sites 0–28 of Fig. 4 are occupied according to the Table. A dash below the 17th row indicates that for the corresponding 17 atom clusters, the atoms 17–28 are removed and are directly connected to the Bethe lattice. A star in the 17th row in F indicates that the cluster F' is obtained by replacing the 17th B atom in cluster F by an A atom.

Site	Cluster E	Occupancy Cluster F	Cluster J
0	A	A	A
1	B	A	B
2	B	A	A
3	A	B	A
4	B	B	A
5	B	B	B
6	B	B	A
7	B	B	A
8	A	B	B
9	B	A	A
10	A	A	B
11	B	A	A
12	A	A	B
13	B	A	B
14	A	B	A
15	A	B	B
16	B	B *	B
–	–	–	–
17	A	A	B
18	A	A	B
19	B	A	A
20	A	B	A
21	B	A	A
22	A	B	A
23	A	B	B
24	B	A	A
25	B	A	B
26	A	A	A
27	A	B	B
28	A	B	B

respectively. In Figs. 5(a), 6(a), and 7(a) we have drawn the density of states corresponding to the clusters of 17 atoms, whereas Figs. 5(b), 6(b) and 7(b) the density of states corresponding to the clusters of 29 atoms is drawn. In Figs. 5–7 show the density of states obtained by Falicov and Ynduraian[10] using a different boundary condition. From the results of our calculation we conclude:

(a) The local configuration is very important in determining the density of states as a comparison of Figs. 5–7 with Fig. 3 reveals. We see that the density of states of Figs. 5(a) and 5(b) corresponding to cluster J are very similar to the density of states at the cluster A-$AAAB$ in Fig. 3. In a similar way Figs. 6(a) and 6(b) (see also Fig. 10) compare with A-$AABB$ in Fig. 3 and Figs. 7(a) and 7(b) compare with cluster A-$ABBB$ in Fig. 3.

(b) The effect of the sixfold rings of bonds in the shape of the density of states is negligible as clearly shown by a direct comparison of Figs. 5(a), 6(a), and 7(a) with Figs. 5(b), 6(b), and 7(b), respectively. The reason for this is that, since the position of the atoms in the alloy is random, there is no constructive coherence of the phases of the wave function as in the perfectly ordered case,[9,13] where the rings have a considerable effect on the density of states.

(c) The shape of the density of states we have obtained is stable against changes in the boundary condition. If we change the concentration in the Bethe lattice, the structures in the density of states do not change. This proves that the boundary condition is good and that the structure we find in the density of states is a real manifestation of local environment.

(d) We can view the cluster as an extended defect embedded in the mean-field Bethe lattice.

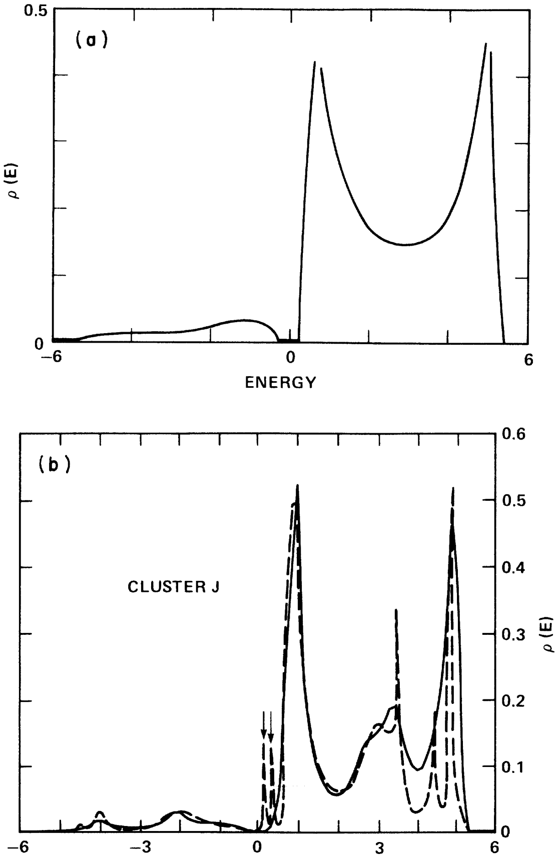

FIG. 5. (a) Local density of states at a central A atom for a 17-atom cluster J, with configuration given in Table I. ($x=0.5, \delta=5$). (b) Same as in Fig. 5(a) for a 29-atom cluster J (solid curve). Dashed curve is that obtained by a different mean-field approximation (Ref. 10). Localized states in the gap, indicated by arrow, have a small strength in our calculation.

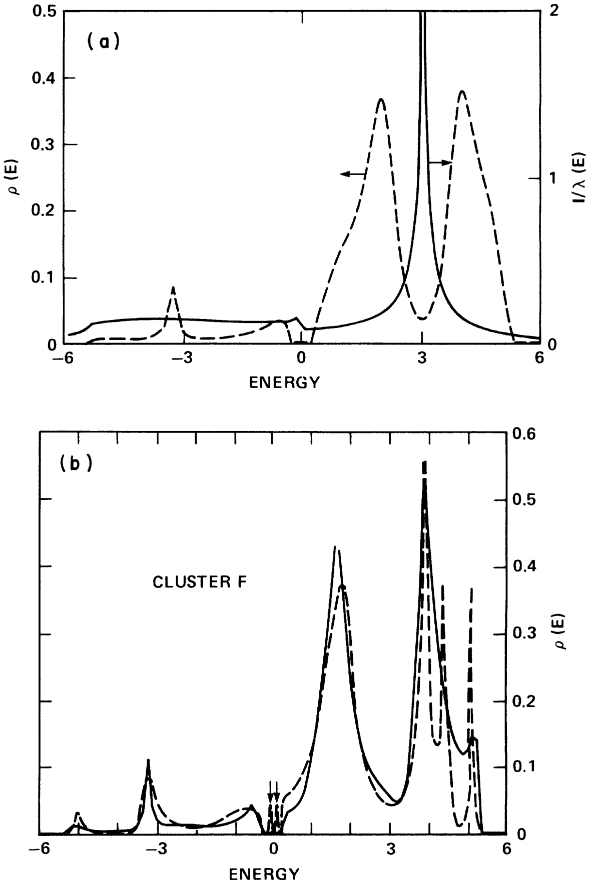

FIG. 6. (a) Local density of states $\rho(E)$ (dashed curve) and localization $1/\lambda$ (solid curve) for 17-atom F cluster. (b) Local density of states of the 29-atom F cluster. Dashed lines are due to Ref. 10. Localized states are shown by arrow.

This produces the states in the gap of the densities of states of the latter (compare Figs. 1 and 2) which are localized in the cluster and decay exponentially into the Bethe lattice. Although their contribution to the density of states is small, the presence of these states in the gap of the CPA density of states shows that the split-band limit[7] in CPA is an artifact of single-site approximation.

B. One-dimensional system

Since our method works for any coordination number, it is rather trivial for us to calculate the densities of states for a one-dimensional system. These are shown in Figs. 8–10 along with Butler's[11] results. Here we restrict ourselves to three-site cluster only. We have calculated the projected densities of states at the central site for all the possible arrangements and then averaged with appropriate weights as given by the concentration. The agreement is clearly very good and obviously would improve with larger clusters. This small cluster has essentially all the peaks seen in the numerical experiment. In Fig. 10, we note that the self-consistent cluster approximation of Butler ran into trouble around $E \sim 8.1$. In our case we do not have any such problem. This clearly demonstrates that the power of our method lies in its simplicity and avoids all the problems of singularity which have marred any previous attempt to go beyond single-site CPA. Whereas Butler's schemes are only for a one-dimensional system, our scheme is good for any dimension and coordination.

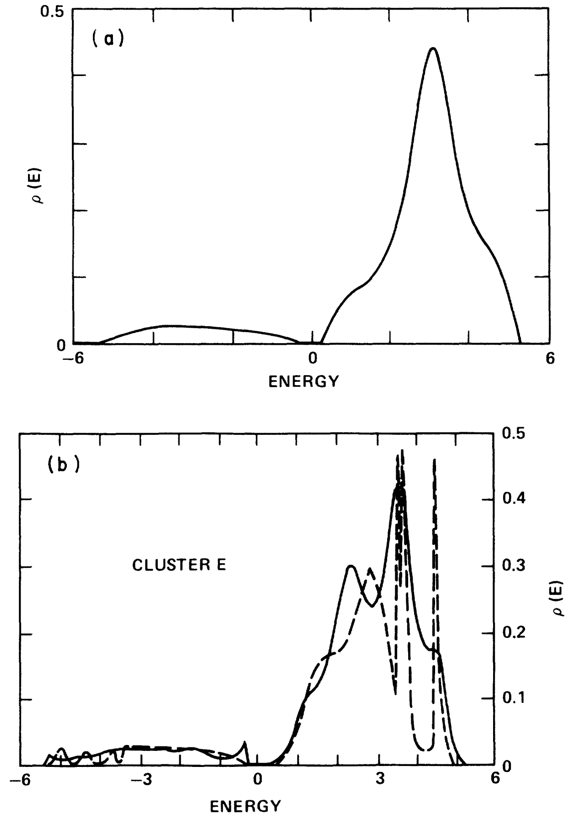

FIG. 7. (a) Local density of states for the 17-atom cluster E. (b) Same as in Fig. 6(b) for the 29-atom cluster E.

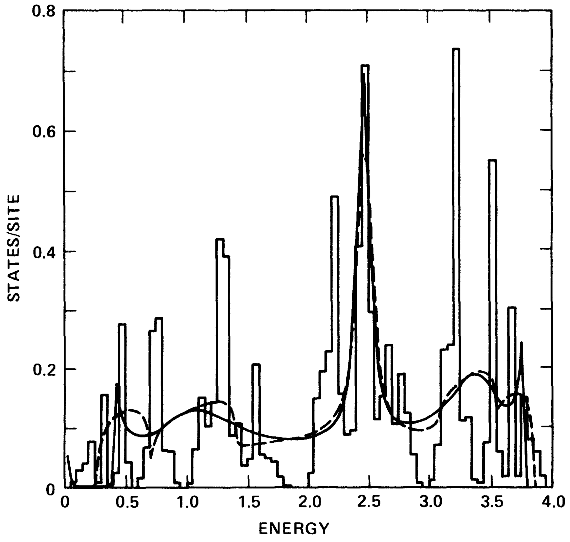

FIG. 8. Average density of states per atom for a three-atom cluster averaged over all possible cluster configurations for a one-dimensional case. Solid curve is our result for $x = 0.5$ and $\delta = 4$ and the dashed curve is that given by Butler along with Smith's histogram (see Fig. 2 of Ref. 11).

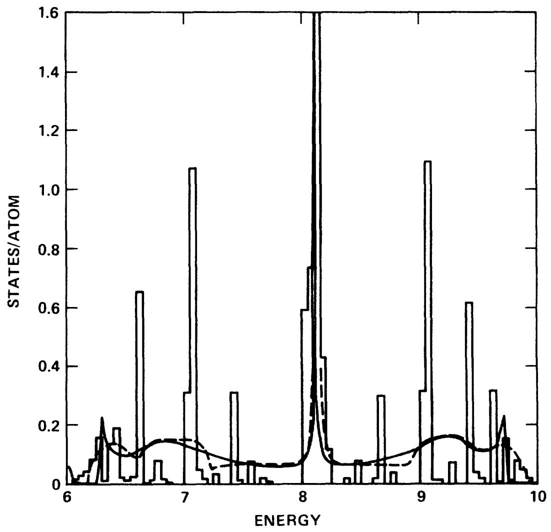

FIG. 9. Same as in Fig. 8 for $x = 0.5$ and $\delta = 16$. (See Fig. 6 of Ref. 11.)

IV. LOCALIZATION

In order to study the localization we follow Papatriantafillou.[12] The matrix element of the Green's function between two different orbital wave functions is given by the following expression:

$$G_{n0}=\sum_i \frac{\phi_n^*(E_i)\,\phi_0(E_i)}{E-E_i+i0}=G_{00}(E)\,F_{n0}(E)\,, \qquad (4.1)$$

which defines $F_{n0}(E)$. $G_{00}(E)$ is given by

$$G_{00}(E)=\sum_i \frac{\phi_0^*(E_i)\,\phi_0(E_i)}{E-E_i}\,, \qquad (4.2)$$

where $\phi_n(E_i)$ denotes the total wave function projected on the nth site at an energy (eigenvalue) E_i. In other words; if

$$H|\psi_i\rangle=E_i|\psi_i\rangle\,, \qquad (4.3)$$

then

$$\phi_n(E_i)=\langle n|\psi_i\rangle\,. \qquad (4.4)$$

From the above equations, if we take the residues at each pole E_i we get

$$F_{n0}(E)=\phi_n(E)/\phi_0(E)\,. \qquad (4.5)$$

Then $F_{n0}(E)$ gives a measure of the localization length, i.e.,

$$\tau_n=(-1/n)\ln|F_{n0}|=1/\lambda \qquad (4.6)$$

denotes the extent of overlap of the zeroth site wave functions at nth site. Clearly, the smaller is the overlap the more confined is the wave function.

Since our method for determining G_{00} yields G_{0n} simultaneously, so we can immediately calculate the quantity τ_n for the different clusters of atoms that we have studied in Sec. III. In addition to the information about the degree of localization, τ_n provides us with a criteria for choosing the size of the cluster so as the boundary condition is almost unimportant. The idea here is to choose the cluster in such a way that τ_n, i.e., the overlap of a central atom and an nth atom at the edge of the cluster is small enough for the range of the energy of interest. Then, in such case, the boundary effects are going to be of secondary importance.

To show how these ideas work in a practical case we have taken the cluster of 17 atoms and have calculated τ_n for different atoms in the cluster. In Fig. 6(a) we have drawn for the cluster F both the local density of states in the central atom and $\lambda=1/\tau_n$; n is the atom labeled 16 (see Fig. 4 and Table I). Suppose now we make the atom of F cluster of Sec. III at site 16 to be of class A instead of class B, and call this a cluster F'. The local density of states for F is frawn in Fig. 10. We see that the overall shape of the density of states for the two clusters F [Fig. 6(a)] and F' is similar; there are two peaks and one dip in the positive energy region. The main difference is that in the cluster F the peaks are sharper than in cluster F'. It is interesting to note that atoms 4, 14, 15, and 16 all belonging to B give rise to a sort of "banner" at the edge of the cluster F and tend to isolate the cluster. This suggests that the wave functions are more localized in the cluster F and the density of states tends to approach to the density of states of an isolated cluster which would be given by a few δ functions. This is clear when we compare τ_{16} for the two clusters in Fig. 8. In the new cluster, τ_{16} is large only when the density of states displays a peak in contrast with what happen in cluster F'.

It is clear that the study of τ_n above cannot tell whether or not a state is localized (this would need need the study of τ_n for very large n), but, on the other hand, as we have shown with the above example, the study of τ_n can give a lot of information about how localized the states are.

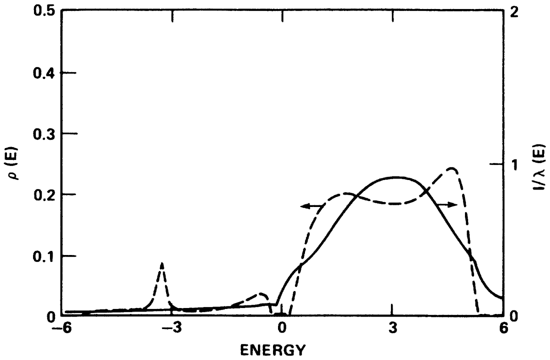

FIG. 10. Local density of states $\rho(E)$ (dashed line), and the localization $1/\lambda(E)$ for a 17-atom cluster F' (see Table I). Compare Fig. 6(a) for the same quantities for the 17-atom cluster F.

V. SUMMARY AND DISCUSSION

In this paper we reported a new method of calculating the densities of states in a disordered material which can have a topological and a substitutional disorder. In amorphous solids, compositional fluctuations ranging from local ordering in the form of a superstructure to phase separation may occur and can be handled by our method. We report here the local densities of states for a three-dimensional fourfold-coordinated binary compound which alone reveal interesting results such as the effects of rings. Also, we have seen that the dominant structures in the densities of states are determined by the local arrangement as is commonly believed for amorphous materials from experimental grounds. An easy way to obtain the densities of states averaged over various clusters would be to generate them by a Monte Carlo technique and average the densities of states. We have compared the density of states, averaged over all possible clusters, for three-site clusters in a one-dimensional system. This agrees quite well with Butler's calculations.[11] Our calculation has the desirable feature of being free from singularities in the self-energy. We have tried to give an estimate of the optimum cluster size in terms of localization length. Clearly, the question of localization in a three-dimensional topologically disordered structure can be studied by our method by considering larger clusters. It would be interesting to study the correlation effects on the localization length. Since we solve the Green's functions for the cluster exactly, it is obvious that one can consider the effect of off-diagonal disorder exactly too. This would amount to solving the set of linear equations for $G_{00}, \ldots, G_{0n}$ with appropriate V_{nm}'s. The boundary again has to be treated in an approximate way. Finally, we have considered here only one orbital per site. It is obvious from the study of Yndurain *et al.*[13] that to extend it to proper *sp* hybridized orbitals is not difficult. Anyway, G_{0j}'s now will be matrices whose components will form a set of linear equations which can be solved rather easily.

---

*Supported by a Fullbright Fellowship under the "Program of Cultural Cooperation between the U.S.A. and Spain."

†Work supported in part by the NSF through grant DMR72-03106-A01.

[1] F. Brouers, F. Ducastelle, F. Gautier, and J. Van Der Rest, J. Phys. F 3, 2120 (1973).

[2] F. Brouers, M. Cyrot, and F. Cyrot-Lackman, Phys. Rev. B 7, 4370 (1973).

[3] L. M. Schwartz, Phys. Rev. B 7, 4425 (1973).

[4] K. Aoi, Solid State Commun. 14, 929 (1974).

[5] K. Aoi, H. Deuling, and K. H. Bennemann, Phys. Rev. B 10, 1975 (1974).

[6] P. Soven, Phys. Rev. 156, 809 (1967).

[7] B. Velický, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968).

[8] F. Yndurain, J. D. Joannopoulos, M. L. Cohen, and L. M. Falicov, Solid State Commun. 15, 617 (1974).

[9] J. D. Joannopoulos and F. Yndurain, Phys. Rev. B 10, 5164 (1974).

[10] F. Yndurain and L. M. Falicow Solid State Commun. 17, 1545 (1975); Phys. Rev. B 12, 5664 (1975).

[11] W. M. Butler, Phys. Rev. B 8, 4499 (1973).

[12] C. Papatriantafillou, Phys. Rev. B 7, 5386 (1973).

[13] F. Yndurain and J. D. Joannopoulos, Phys. Rev. B 11, 2957 (1975).