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THE "CLUSTER-BETHE" METHOD: ELECTRONIC DENSITY OF STATES OF AMORPHOUS AND CRYSTALLINE HOMOPOLAR SOLIDS

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ABSTRACT

A new method is developed to study the electronic density of states of infinite networks of atoms. The method involves treating part of the system exactly as a cluster and simulating the effects of the rest of the environment by connecting a Bethe lattice (Cayley tree) to the surface of the cluster. Calculations show that the local ring-like topologies of each atom are of primary importance in determining structure in the electronic density of states. The densities of states of the diamond, BC-8 and ST-12 structures are studied in detail using this method. These calculations are in excellent agreement with the exact results. Because of this, the method is used to obtain the density of states of the Polk and Connell random network models. These models give the same radial distribution functions but exhibit striking differences in their densities of states which are interpreted in terms of topology.

I. Introduction

There are many theoretical problems in solid state physics which defy the use of simplifications found in

treating systems with complete periodicity. The fields of surfaces and amorphous solids are certainly two very large areas involved with problems of this type. This is particularly true in the study of amorphous solids where Bloch's theorem is no longer valid. One is thus presented with a severe obstacle in trying to formulate any type of realistic theory, a realistic theory being one which can be readily compared with experiment.

Recently the study of amorphous semiconductors (e.g., Ge, Si, GaAs, etc.) has been concerned to a large extent with the structural nature of the amorphous phase and with the effects of disorder on the electronic density of states (DOS). The DOS is a particularly useful tool in studying the structural nature of amorphous systems because it is a simple, well defined function and is quite sensitive to disorder and topology. Experimentally, information about the DOS can be obtained from ultra-violet (UPS)[1,2] and X-ray (XPS)[2,3] photoemission spectroscopy as well as from X-ray emission and absorption measurements[4]. In the case of Ge and Si these experiments reveal that the DOS in the amorphous phase consists of a smoothed blue-shifted peak relative to the crystal phase at the top of the valence band ("p-like" states) and a seemingly large broad peak at the bottom of the valence band ("s-like" states). This is in contrast to the two strong peaks found in the "s-like" region

of the DOS of the crystalline phase.

There have been many theoretical approaches in the study of the amorphous problem. A very fruitful approach[5] has been to discern information about the amorphous phase by studying various complex crystalline metastable phases (e.g., the BC-8 and ST-12 structures) which contain many atoms in a primitive cell. These calculations have revealed the importance of short range disorder in accounting for the behavior of the amorphous spectra. Other approaches have been to study finite clusters of atoms where long-range order has been eliminated completely. One approach[6] is to calculate the DOS by using moments obtained by counting paths determined by the type of Hamiltonian one is using. This method is quite interesting but it is of limited use because of the large number of moments needed before any structure in the DOS can be believed. Another approach[7,8] is to calculate the DOS for a finite cluster of atoms with some type of boundary condition to take care of the surface atoms. The problem here is that again one needs to go to large clusters of atoms because of the difficulty in applying reasonable boundary conditions without getting spurious results. Yet another approach[9] has been to study simple models without periodicity which (for some simple Hamil-

tonians) are exactly soluble like the Bethe lattice [10] (Cayley tree) and the Husumi cacti [11]. The DOS of these models however are relatively featureless so that taken alone they provide little new insight into the problem.

In this paper, we present a new method [12] to obtain the DOS of an infinite connected network of atoms in terms of the local density of states (LDOS) of each atom at the center of a small cluster of this system. The method essentially entails treating part of the system exactly (i.e. as a cluster) and replacing the rest of the environment by an appropriate Bethe lattice. The details are discussed in Section II.

The Hamiltonian that we will be using is of the form

$$H = V \sum_{i,i'} |i\rangle\langle i'| \quad , \qquad (1)$$

where $|i\rangle$ represents an "s-like" orbital on atom i and V is the interaction between nearest neighbor orbitals. This Hamiltonian is used because of its simplicity and and because its eigenvalues are related by an analytic transformation [13] to the "s-like" states of a four-orbital Hamiltonian where one places four sp^3-like orbitals on each atom and takes two types of interactions into account [14].

These interactions consist of V_1 between different orbitals on the same atom and V_2 between orbitals on different atoms but along the same bond. This four-orbital Hamiltonian is very useful since it gives a reasonably good description of the "s-like" states of more realistic Hamiltonians. Moreover, the one-orbital (eq. 1) and four-orbital Hamiltonians allow us to calculate the LDOS of an atom in a "cluster-Bethe" system exactly.

The format of the paper is as follows. In Section II we discuss the details of our method. This includes the way of choosing a cluster and the physical and mathematical reasons for using the Bethe lattice to simulate the effects of an infinite system. We then apply our method with some simple examples which reveal the importance of <u>local</u> topologies in determining the type of structure found in the "s-like" region of the DOS. In particular we are able to show decisively that this structure is intimately related to the numbers and types of rings of bonds in the vicinity of and passing through each atom. In Section III we test our method as a calculational tool by applying it to the BC-8 and ST-12 structures. We then examine two popular structural models (the Polk[15] and Connell[16] models)

which give very similar radial distribution functions[16] but differ in that the Polk model contains even and odd membered rings of bonds whereas the Connell model contains only even membered rings of bonds. Next in Section IV we discuss the properties of finite clusters and the effects of the Bethe lattice on the band edges. Finally, in Section V we make some concluding remarks.

II. The "Cluster-Bethe" Method

In this section we describe and discuss the method used in obtaining the DOS. The idea is the following. We consider any infinite connected network of atoms with four-fold coordination and we choose one atom as a reference point. We then remove a small cluster surrounding and including this atom from the system. The cluster is chosen such that every atom in the cluster is part of at least one ring passsing through the central or reference atom. A Bethe lattice is now introduced and connected to the surface atoms to simulate the effects of the rest of the original system. The Bethe lattice is an infinite connected network of atoms with four-fold coordination but with no rings of bonds. If we now use the one-orbital or four-orbital

Hamiltonian (described in the Introduction) we can solve for the LDOS of the central atom in the "cluster-Bethe" system analytically.

The reasons for using the Bethe lattice as a boundary condition are threefold. Firstly, from a mathematical point of view we can solve the system exactly. Secondly, from a physical point of view we preserve the connectivity of the system and we maintain the four-fold coordination. And finally, the DOS of the Bethe lattice is smooth and featureless. Consequently, any structure found in the LDOS of an atom in the "cluster-Bethe" system is very closely associated with the local environment of this atom.

The calculational procedure is as follows. The DOS in a Green function formalism is given simply by

$$n(E) = -\frac{1}{\pi}\,\mathrm{Im}[\mathrm{Tr}G(E)] \qquad (2)$$

and we are interested in obtaining the diagonal matrix elements of G(E).

We can write G(E) as a Dyson equation

$$G = \frac{1}{E-H} = \frac{1}{E} + \frac{1}{E}HG \quad , \qquad (3)$$

so that by taking matrix elements between a basis set

$\{|i\rangle\}$ we obtain

$$E \langle i|G|j\rangle = \delta_{ij} + \sum_n \langle i|H|n\rangle\langle n|G|j\rangle \quad . \qquad (4)$$

The LDOS $n_i(E)$ of the ith atom is then given by

$$n_i(E) = -\frac{1}{\pi} \mathrm{Im} \langle i|G|i\rangle \qquad (5)$$

and

$$n(E) = \sum_i n_i(E) \ , \qquad (6)$$

where n(E) is the total density of states.

As a simple example of how our method works, let us consider a cluster of atoms in the diamond structure shown in Figure 1. The reference atom is labelled 0 and from symmetry many atoms are equivalent and are labelled with the same number. Thus there are only four inequivalent atoms in this cluster of 29 atoms. Furthermore, we notice that there are twelve six-fold rings of bonds passing through the central atom. We now construct a "diamond-Bethe" system by connecting a Bethe lattice to the dangling bonds of atoms 2 and 3. For simplicity, let us label all the atoms in the Bethe lattices connected to atoms 2 and 3 by only even and only odd numbers respectively. The LDOS of atom 0 can now be solved by using equation (4) with H being a one-

orbital Hamiltonian with only nearest neighbor interactions V as in (1). We then obtain the following infinite set of linear equations

$$
\begin{aligned}
E\langle 0|G|0\rangle &= 1 + 4V\langle 1|G|0\rangle \\
E\langle 1|G|0\rangle &= V\langle 0|G|0\rangle + 3V\langle 2|G|0\rangle \\
E\langle 2|G|0\rangle &= V\langle 1|G|0\rangle + 2V\langle 3|G|0\rangle + V\langle 4|G|0\rangle \\
E\langle 3|G|0\rangle &= 2V\langle 2|G|0\rangle + 2V\langle 5|G|0\rangle \\
E\langle 4|G|0\rangle &= V\langle 2|G|0\rangle + 3V\langle 6|G|0\rangle \\
E\langle 5|G|0\rangle &= V\langle 3|G|0\rangle + 3V\langle 7|G|0\rangle \qquad (7) \\
&\vdots \\
E\langle 2N|G|0\rangle &= V\langle 2N-2|G|0\rangle + 3V\langle 2N+2|G|0\rangle \\
E\langle 2N+1|G|0\rangle &= V\langle 2N-1|G|0\rangle + 3V\langle 2N+3|G|0\rangle \\
&\vdots
\end{aligned}
$$

These equations can be solved using the transfer matrix technique. We define

$$T = \langle N+2|G|0\rangle \,/\, \langle N|G|0\rangle \;; \quad N \geq 2 \,, \qquad (8)$$

so that we can reduce the infinite set of equations in (7) to the following four linear equations

$$
\begin{aligned}
E\langle 0|G|0\rangle &= 1 + 4V\langle 1|G|0\rangle \\
E\langle 1|G|0\rangle &= V\langle 0|G|0\rangle + 3V\langle 2|G|0\rangle \\
E\langle 2|G|0\rangle &= V\langle 1|G|0\rangle + 2V\langle 3|G|0\rangle + VT\langle 2|G|0\rangle \\
E\langle 3|G|0\rangle &= 2V\langle 2|G|0\rangle + 2VT\langle 3|G|0\rangle
\end{aligned}
\tag{9}
$$

where, from (7) and (8)

$$T = [E-(E^2-12V^2)^{1/2}] \,/\, 6V \quad . \tag{10}$$

The analytic solution to the above system gives

$$
\begin{aligned}
n_o(E) &= -\frac{1}{\pi}\,\mathrm{Im}\langle 0|G|0\rangle = \\
&-\frac{1}{\pi}\,\mathrm{Im}\{E-4V^2[E-3V^2(E-VT)^{-1}\Sigma^{-1}]^{-1}\}^{-1} \quad ,
\end{aligned}
\tag{11}
$$

where

$$\Sigma = 1 - 4V^2(E-2VT)^{-1}(E-VT)^{-1} \quad . \tag{12}$$

The result (11) is plotted in Figure 2(a) as a thick solid line. In Figure 2(b) we plot the corresponding results using the four-orbital Hamiltonian. First of all we notice that even for this small cluster of only 29 atoms we get structure in the LDOS which is very different from that of the Bethe lattice shown superimposed as a dashed line. Secondly, we notice that the LDOS of the "diamond-Bethe" system is rather similar to the LDOS of an atom in

the diamond structure (shown as a thin solid line). This emphasizes the importance of short range configurations in determining structure in the DOS. In particular the two peaks and the dip in the middle of the spectrum can be interpreted in terms of the twelve six-fold rings passsing through the central atom. To show the association of structure in the DOS with the ring statistics of a cluster we have done the following. Five "cluster-Bethe" systems were constructed such that each cluster contained six rings of <u>only one type</u> (i.e. 6 five-fold, six-fold, seven-fold, and eight-fold rings respectively). These clusters were made so that there was one ring in each pair of bonds of the central atom. The results are shown in Figures 2(c) and (d) using the one-orbital and four-orbital Hamiltonians respectively. The structure in these DOS can be very easily identified with the eigenvalues of isolated rings as shown in Figure 2(e). The agreement is excellent and indicates that the ring-like nature of the local environment is essential in determining the type of structure found in the DOS. Moreover, a close examination of Figure 2(c) shows that the strengths of the peaks are much larger the smaller the ring. This indicates the importance of the smallest rings in a cluster. Finally, the bigger peak to dip ratio in the spectrum of the "diamond-

Bethe" system as compared to the spectrum of the "six-fold ring cluster-Bethe" system is caused by the larger number of six-fold rings in the former system. This indicates the importance of the number of rings of a given type in determining the sharpness of the structure in the DOS.

Before concluding this section, two specific comments about the "cluster-Bethe" method should be made. Firstly, it is interesting to discuss the relationship between our approach and the Haydock, Heine and Kelly (HHK) method [17]. In this method, the local Green function of an atom is expanded as a continued fraction with the mathematical boundary condition that all the coefficients are constant beyond a certain term. The Bethe lattice, however, taken alone can also be expanded as a continued fraction with constant coefficients. Nevertheless, a close inspection shows that the local Green function of an atom in a <u>cluster-Bethe system</u> can by no means be reduced to the HHK form. Moreover, there is no physical similarity between the two methods since HHK deal with a finite cluster whereas we deal with an infinite system. Secondly, it might be aruged that the effects of the Bethe lattice are nothing but a broadening of the LDOS of a bare cluster. This, however, is not the case as we shall see with several examples in the next sections.

III. A Study of Densities-of-States

Using the "cluster-Bethe" method we examine and analyse the DOS of the BC-8 and ST-12 structures [5] and we calculate the DOS of the Polk [15] and Connell [16] models. The BC-8 and ST-12 structures have been shown [5] to be very important in studying the structural aspects of the amorphous Group IV elements. They contain 8 and 12 atoms in a primitive cell respectively and have very different ring-like topologies. The BC-8 and ST-12 structures also provide us with two prototypes which can be used to check our method as a calculational technique. We can construct various "BC-8 and ST-12 Bethe" systems with clusters of different sizes. By comparing the DOS of these systems with the Bloch DOS of the BC-8 and ST-12 structures we can examine how our method converges to the exact solution. This gives us important information about the limits and validity of our method. With this knowledge at hand we proceed to study two popular structural models of the amorphous phase; the Polk and Connell models.

A. BC-8

In the BC-8 structure we only have even-numbered rings

of bonds and only one type of atom. Consequently, as in diamond, the LDOS and the total DOS are equivalent. In Figure 3 we have plotted the LDOS of four "BC-8-Bethe" systems using the one-orbital [(a), (c), (e) and (g)], and four-orbital [(b), (d), (f) and (h)] Hamiltonians. In Figure 3(a) and Figure 3(b) (dashed line) we show the results corresponding to a BC-8 cluster with only 26 atoms. This cluster contains 9 six-fold rings passing through the central atom and is the smallest cluster that can be made such that the central atom is not directly connected to a Bethe-lattice. The solid line in Figure 3(b) is the Bloch DOS of the BC-8 crystal obtained with a band structure calculation. In Figures 3(c) and (d), (e) and (f), and (g) and (h), we have plotted the LDOS of "BC-8-Bethe" systems with clusters containing up to and including all eight-fold, ten-fold and twelve-fold rings respectively passing through the central atom.

Let us now examine the trends as we go down the columns in Figure 3. We notice first that the general features of the Bloch DOS are already present when dealing with the smallest cluster of atoms. We see that the BC-8 crystal displays a spectrum which can be essentially characterized in terms of two strong peaks and one dip in the middle. In the 26-atom cluster these two peaks can be directly identified with the 9 six-fold rings passing through the central atom.

This is easily seen by comparing Figures 3(a) and (b) with Figures 2(c) and (d) respectively. When we increase the number of atoms in the clusters we get more structure in the DOS but the general features of two peaks and a dip in the middle still remain. In Figures 3(c) and (d) we notice that there is a small hump in the middle of the spectra. This is caused by the large number (36) of 8-fold rings passing through the central atom. In the case of Figure 3(e) and (f) we have a cluster with 113 atoms and the results are very similar to the exact result shown in Figure 3(b). It is now fruitless to carry the ring interpretation further to larger rings. However, the important point is that the six-fold ring character still persists. For the cluster in Figures 3(g) and (h) we have 207 atoms and now our method can even resolve the wiggles in the middle of the spectrum. The only discrepancies with the exact result are the small peaks near the band edges. These will be discussed at length in Section IV.

B. ST-12

The ST-12 structure is very useful because it provides us with a system with 12 atoms in a primitive cell so that effects caused by periodicity should be less important than

for other structures. Furthermore, the ST-12 structure is interesting because it contains five-, six-, seven- and eight-fold rings of bonds. There are two types of atoms in the primitive cell with 4 atoms of Type I and 8 atoms of Type II. In order to compare the DOS of "ST-12-Bethe" systems with the total Bloch density of states of ST-12 we need to construct clusters for each type of atom. In what follows we show only a weighted average of the LDOS of clusters centered on atoms of Type I and II. For a more detailed exposition see Yndurain et al [12]. In Figure 4 we have plotted the DOS (averaged over two atoms) of three "ST-12-Bethe" systems using the one-orbital [(a), (c), and (e)] and four-orbital [(b), (d), and (f)] Hamiltonians. In Figure 4(a) and (b)(dashed line), we show the results corresponding to an ST-12 system with 27 atoms in a Type I cluster and 31 atoms in a Type II cluster. These clusters were chosen so that all five-, six-, and seven-fold rings were included. In the cluster with a Type I central atom we have 4 five-fold, 2 six-fold, 4 seven-fold and 3 eight-fold rings of bonds passing through the central atom. In the cluster with a Type II central atom, we have 3 five-fold, 2 six-fold, 5 seven-fold and 8 eight-fold rings of bonds. If we compare Figures 4(a) and (b) with Figures 2(c) and (d) respectively, we find that the peak near -2.7V is caused by a five-fold ring peak and the overlap of a seven- and eight-fold ring peak. The little bump near -1.6V is caused

mostly by a six-fold ring peak while the hump around 0V is caused primarily by an eight-fold ring peak and the overlap of a five- and seven-fold ring peak. Finally, the peak around 2V includes the overlap of five-, six-, seven-, and eight-fold ring peaks.

We notice again as in the BC-8 structure the general features of the Bloch DOS of the ST-12 structure (shown as a solid line in Figure 4(b)) are already present when dealing with a very small cluster of atoms. When we add more atoms to the clusters, we are able to resolve the various peaks more clearly. In Figures 4(c) and (d), and (e) and (f), we have plotted the DOS of "ST-12-Bethe" systems with clusters containing up to and including all eight-fold and ten-fold rings respectively, passing through the central atom. This saturates the number of eight-fold rings to a total of 22 and 25 for atoms of Type I and Type II respectively. This saturation causes a sharpening of the structure as is seen in Figures 4(c) and (d). Finally, in Figures 4(e) and (f), we obtain DOS spectra for clusters with only 93 atoms which are in excellent agreement with the Bloch DOS of ST-12. Every peak is resolved and even the shape of the structure is reproduced.

This agreement is very important in testing the "cluster-Bethe" method as a calculational technique. What we have found is that we can proceed with confidence and reliability to

study any amorphous system of atoms. As long as we choose clusters containing up to ten-fold rings of bonds, we are assured to obtain a spectrum which will be in very good agreement with the exact result. With this in mind we proceed in the next part to study some structural models of an amorphous random network.

C. Structural Models

We will now use the "cluster-Bethe" method to study the Polk [15] and Connell [16] models. These are structural models of an amorphous tetrahedrally coordinated solid which have some very interesting similarities and differences. They are both models of an amorphous random network and both give radial distribution functions which are in very good agreement with experiment. However, they have very different topological properties. The Polk model represents a system with odd and even numbered rings of bonds whereas the Connell model is constructed so that there are only even numbered rings of bonds. The atoms in these models are all inequivalent so that in principle we would need to average over the LDOS of every atom to obtain the total DOS. For the Connell model, however, we found that the LDOS of the atoms studied were very similar. This is caused by the

strong similarity in the ring statistics of these atoms, as shown in Table I. Therefore in Figure 5 we show a DOS averaged over only 5 central atoms in the Connell random network. Again we use the one- and four-orbital Hamiltonians. In Figure 5(a) and (b), and (c) and (d), we have plotted the DOS of two "Connell-cluster-Bethe" systems with clusters containing up to and including all eight-fold and ten-fold rings respectively. These clusters contain a central atom which on the average (see Table I) has 16 six-fold rings and 21.6 eight-fold rings. This is a very large number of six-fold rings and this is reflected clearly as a very large dip at the middle of the spectrum with two large peaks near the band edges. This, however, is quite different from what happens in amorphous Ge or Si where we get a substantial filling up of the dip[3]. Although the Connell model does not seem to be appropriate for amorphous Ge or Si, it may still be valid for the amorphous III-V compounds (as the authors intended).

Let us now examine the Polk model. For this system we found that the LDOS of the atoms were not very similar. This is also reflected in the ring statistics as shown in Table II. In Figure 6 we have plotted the LDOS of two "cluster-Bethe" systems for three different atoms in the Polk model using the one-orbital [(a), (c), and (e)] and

four-orbital [(b), (d), and (f)] Hamiltonians. In Figure 6(a) and (b) we show the LDOS of an atom (label 229) containing 1 five-fold, 9 six-fold, 4 four-fold, and 16 eight-fold rings of bonds in a cluster containing up to and including all eight-fold rings (dashed line) and all ten-fold rings (solid line). In Figure 6(c) and (d) we show the LDOS of another atom (label 223) in two similar clusters containing 2 five-fold, 6 six-fold, 5 seven-fold and 17 eight-fold rings of bonds. Finally, in Figure 6(e) and (f) we show the LDOS of an atom (label 231) with ring statistics given by 3 five-fold, 4 six-fold, 7 seven-fold and 21 eight-fold rings of bonds. Comparing the spectra as we go down the columns we find again a correlation between structure in the DOS and ring statistics. For the DOS on the top we notice a large characteristic dip in the middle of the spectrum. This dip becomes gradually filled in until we get to the DOS at the bottom where we now get a peak in the middle of the spectrum. This behavior is easily correlated with the changes in ring statistics as we go down the columns in Figure 6. The ring statistics of the atom at the top of the figure show a very small number of five- and seven-fold rings but a relatively large number of six-fold rings. Thus, we get a characteristic two-peak

and dip structure. As we go down the columns, there is an increasing number of five-, seven- and eight-fold rings while the number of six-fold rings is decreasing. This is reflected as an introduction of new structure near the middle of the spectrum.

In Figure 7 we show a DOS averaged over 17 central atoms in the Polk model, using the one-orbital and four-orbital Hamiltonians. In Figure 7(a) and (b), and (c) and (d) we have plotted the DOS of two "Polk-cluster-Bethe" systems with clusters containing up to and including all eight-fold and ten-fold rings respectively. Comparing Figure 7 with Figure 5, we notice the striking difference between the Polk and Connell models when using the DOS as a discerning factor. The Polk model seems to be a good model for the amorphous phase of Ge and Si even though we only have a partial filling up of the dip. It remains to be seen from future high resolution spectroscopy whether the amorphous phase really has a partial or complete filling up of the dip. This should have important consequences regarding the ring statistics of the amorphous phase.

IV. Finite Clusters and Band Edges

Until now we have been concerned with the position and number of peaks and dips on the DOS. However, we have said nothing about the properties of finite clusters and band edges. This is because these properties require a more careful and detailed analysis.

Let us being by examining what we really mean by a LDOS. The LDOS as defined in equation (5) can be written as

$$n_i(E) = \sum_T |\langle\phi_i|\Psi_T\rangle|^2 \; \delta(E-E_T) \quad , \tag{13}$$

where $|\phi_i\rangle$ is the orbital of the ith atom and $|\Psi_T\rangle$ is an eigenfunction of the total system with energy E_T. Equation (13) can also be written as

$$n_i(E) = \frac{\sum_T |\langle\phi_i|\Psi_T\rangle|^2 \; \delta(E-E_T)}{\sum_T \delta(E-E_T)} \sum_T \delta\,(E-E_T) \tag{14}$$

$$n_i(E) = P(E)\; n(E) \tag{15}$$

where n(E) is the total DOS and is equal to $\sum_T \delta(E-E_T)$. From the equation (15) we notice that the LDOS $n_i(E)$ is

just equal to the total DOS multiplied by a weighting function P(E). P(E) is just the average probability that an electron is at the site i when it has an energy E.

The total DOS of a "cluster-Bethe" system is necessarily equal to that of the infinite Bethe lattice. The DOS of the Bethe lattice, however, is only defined in the interval [$-\sqrt{12}$ V, $\sqrt{12}$ V] where V is the interaction parameter of the one-orbital Hamiltonian. If we assume this parameter V has the same value throughout the whole "cluster-Bethe" system, the LDOS of the reference atom is then different from zero only within [$-\sqrt{12}$ V, $\sqrt{12}$ V]. Therefore we cannot for example obtain the correct band edge for the diamond or BC-8 structures which normally would lie in the interval [-4V,4V]. The effects of the Bethe lattice may then be to produce spurious peaks near the band edges. To remedy this situation we took $V = \frac{4V}{\sqrt{12}}$ for the Bethe lattice and V=V in the cluster. This gives us a spectrum that now generally lies in the interval [-4V,4V]. An example of this is shown in Figure 8. The dotted curve in this figure corresponds to the "BC-8-Bethe" spectrum shown in Figure 3(e). Superimposed in Figure 8, we have a solid curve which represents the new "BC-8-Bethe" spectrum with two interaction parameters. We notice that the curves are

almost identical except near the band edges. In fact, the new spectrum looks much more like the exact result (Figure 3(b)) which does not have the small peaks near ± 3V. We obtain similar results for the small peaks near ± 3V in the Connell model shown in Figure 5 (c). In the ST-12 structure, however, these peaks remain essentially unchanged. It is interesting that even for the BC-8 structure these peaks do not vanish completely when we change the strength of the Bethe lattice. We believe this is a real effect which is caused by an intrinsic property of the finite cluster that we are dealing with.

It would be appropriate at this time to examine the Bethe lattice as a boundary condition by comparing the LDOS of "cluster-Bethe" systems with the LDOS of finite isolated cluster systems. In Figure 9 we show the LDOS of three clusters using the one-orbital Hamiltonian with [(a), (c), and (e)] and without [(b), (d), and (f)] the Bethe lattice as a boundary condition. The clusters in (a), (c) and (e) correspond to those shown in Figure 3(a), (c) and (e). The spectra in Figure 9(b), (d) and (f) have been Gaussian broadened by about 0.2V. The differences between the respective spectra in the first and second columns is striking. As we mentioned earlier, the effect of the Bethe lattice cannot be viewed as just an averaging or broadening of a

finite cluster spectrum. For instance, the two strong peaks in the isolated cluster (Figure 9(f)) are not at the correct energies for the total DOS whereas the ones in the "cluster-Bethe" model (Figure 9(e)) are.

Finally we should say a few words about how the "cluster-Bethe" method converges to the exact result for systems with high symmetry. As an example, let us take the diamond structure. The detailed shape of the diamond DOS is governed by Van Hove singularities. For instance, using the one-orbital Hamiltonian, these sharp features occur at 0V, ± 2V and ± 4V (Figure 2(a)). As we take larger and larger "cluster-Bethe" systems we find that the basic two-peak and dip structure remains essentially unchanged, with additional wiggles appearing near the singularities. What is happening here is similar to the Gibb's phenomenon. In addition, we are trying to reproduce the crystalline DOS with an infinite number of delta functions of which only a small number are directly related to the cluster. For example, in the cluster without a Bethe lattice we would get as many delta functions as there are atoms. However, in systems with high symmetry we find that many of these delta functions are degenerate. For instance, in Figure 1, we have a cluster of 29 atoms in the diamond structure. But we only get 4 delta functions since we only have 4 dis-

tinct atoms. Because of these effects the convergence for the diamond structure is rather slow. However, for more complicated structures the convergence is very good. This is clear as we have already seen in the BC-8 and ST-12 structures. Therefore, the "cluster-Bethe" system should have the fastest convergence for amorphous systems.

V. Summary and Conclusions

We have used a new method to study the DOS of infinite systems of atoms by treating part of the system exactly (as a cluster) and letting the Bethe lattice simulate the effects of the rest of the environment. Using this method we have shown the importance of local ring-like-topologies in determining structure in the DOS. By taking various BC-8 and ST-12 "cluster-Bethe" systems we have interpreted the DOS of their crystalline phases. As the size of the clusters increase, more details appear in the DOS spectra, but the basic features are already present in very small clusters of atoms. Consequently, the interpretation of structure in the DOS can be carried

out in terms of small membered rings only. In this way, we have also been able to test our method as a calculational tool by examining how it converges to the exact result. In particular we have found that the convergence is fastest the more complicated the system. For the BC-8, ST-12 and amorphous phases a "cluster-Bethe" system with a cluster containing up to all rings of order ten should give an excellent estimate of the actual DOS.

In this context we have studied two popular structural models of an amorphous random network. Although both models fit the experimental radial distribution functions quite well, their respective DOS is quite different. This is a consequence of their very different ring topologies. One model has only even-numbered rings of bonds while the other has in addition odd-numbered rings of bonds. This shows the sensitivity of the DOS, and hence the usefulness of characterizing amorphous samples, to the <u>local</u> ring topologies of each atom.

Finally, we have found that possible spurious results near the band edges can be eliminated by taking two types of interactions into account when studying a "cluster-Bethe" system using the one-orbital Hamiltonian. By taking the Bethe lattice to have a stronger interaction parameter than

the cluster, the width of the DOS spectrum increases and approaches that of the original system.

There are many extensions and areas where we could apply our method. For example, we are currently extending this method to be used with more realistic Hamiltonians. In particular, we are studying a three parameter molecular orbital tight-binding Hamiltonian and a five parameter four-orbital Hamiltonian. These Hamiltonians can give valence band DOS which are in excellent agreement with experiment.

Our method can be used to study amorphous binary compounds or surfaces on amorphous or crystalline solids. We can also study the effects of impurities. In addition with straightforward extensions to include Bethe lattices of other coordination numbers, we can have a very interesting method of studying amorphous alloys.

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We would like to thank Professor L. Falicov and Professor M.L. Cohen for many useful discussions. We would also like to thank Dr. D. Polk and Dr. N. Connell for sending us the coordinates of their models. Work supported in part by the U.S. Atomic Energy Commission.

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TABLE I

The ring statistics of five atoms near the center of the Connell random network model. A number in the first column represents the label of an atom in the model. The numbers in the second, third, fourth and fifth columns represent the number of five-, six-, seven-, and eight-fold rings of bonds respectively, passing through this atom. A ring is not recognized if more than two atoms in this ring are connected directly to the reference atom.

Label of atom	Number of five-fold rings	Number of six-fold rings	Number of seven-fold rings	Number of eight-fold rings
1	0	18	0	22
2	0	15	0	19
3	0	18	0	22
9	0	15	0	22
10	0	14	0	23

TABLE II

The ring statistics of seventeen atoms near the center of the Polk random network model. The convention is the same as in Table I.

Label of atom	Number of five-fold rings	Number of six-fold rings	Number of seven-fold rings	Number of eight-fold rings
229	1	9	4	16
223	2	6	5	17
231	3	4	7	21
224	1	7	6	14
233	2	4	6	17
232	2	6	5	21
228	1	7	6	12
225	1	8	6	14
236	1	9	6	12
227	3	5	5	12
243	2	6	9	12
8	1	8	3	15
239	4	2	8	14
124	1	7	6	20
234	4	2	7	12
235	1	8	5	12
252	1	6	8	12

FIGURE CAPTIONS

Figure 1 Cluster of atoms in the diamond structure. The central or reference atom is labelled 0. All equivalent atoms are labelled with the same number. The Bethe lattice is connected to the one and two dangling bonds of atoms 2 and 3 respectively.

Figure 2 Density-of-states calculations for the diamond and ring cluster structures. (a) One orbital Hamiltonian in the diamond structure (light full line), Bethe lattice (dashed line) and our results (heavy full line). (b) Four orbital Hamiltonian in the diamond structure (light full line), Bethe lattice (dashed line) and our results (heavy full line). (c) Structure with 6 n-fold rings around the central atom in the one-orbital Hamiltonian: 5 (dashed line) n=5; 6 (solid line) n=6; 7 (dotted line) n=7; 8 (broken line) n=8. (d) Structure with 6 n-fold rings in the four-orbital Hamiltonian. Notation as in (c). (e) The orbital energies for isolated five-fold rings (dashed lines), six-fold rings (solid lines), seven-fold rings (dotted lines) and eight-fold rings (broken lines). The energy in parts (a), (c) and (e) is in units of V (see equation (1)) and the energy in parts (b) and (d) is in eV.

Figure 3 Densities-of-states calculations for four "BC-8-Bethe" systems using the one-orbital [(a), (c), (e) and (g)] and four-orbital [(b), (d), (f), and (h)] Hamiltonians. (a) and (b) (dashed line); the LDOS for a "BC-8-Bethe" system with a cluster containing all rings up to order six passing through the central atom. The full line in (b) is the DOS for the BC-8 structure. (c) and (d) the LDOS for a "BC-8-Bethe" system with a cluster containing all rings up to order eight passing through the central atom. (e) and (f) the LDOS for a "BC-8-Bethe" system with a cluster containing all rings up to order twelve passing through the central atom. (g) and (h) the LDOS for a "BC-8-Bethe" system with a cluster containing all rings up to order twelve passing through the central atom. The energy is in units of V for (a), (c), (e) and (g) and in units of eV for (b), (d), (f) and (h).

Figure 4 Densities-of-states averaged over two atoms for three "ST-12-Bethe" systems using the one-orbital [(a), (c) and (e)] and four-orbital [(b), (d), and (f)] Hamiltonians. (a) and (b) (dashed line); the DOS for an "ST-12-Bethe" system with a cluster containing all rings up to order seven passing through the central atom. The full line in (b) is the total DOS for the ST-12 structure. (c) and (d) the DOS for an "ST-12-Bethe" system with a cluster containing all rings up to order eight passing

through the central atom. (e) and (f) the DOS for an "ST-12-Bethe" system with a cluster cont ining all rings up to order ten passing through the central atom. The energy is in units of V for (a), (c) and (e), and in units of eV for (b), (d), and (f).

Figure 5 Densities-of-states averaged over five atoms near the center of the Connell model for two "Connell-cluster-Bethe" systems using the one-orbital [(a) and (c)] and four-orbital [(b) and (d)] Hamiltonians. (a) and (b) the DOS for a "Connell-cluster-Bethe" system with a cluster containing all rings up to order eight passing through the central atom. (c) and (d) the DOS for a "Connell-cluster-Bethe" system with a cluster containing all rings up to order ten passing through the central atom. The energy is in units of V for (a) and (c) and in units of eV for (b) and (d).

Figure 6 Densities-of-states for three atoms in the Polk model using the "cluster-Bethe" method with the one-orbital [(a), (c) and (e)] and four-orbital [(b), (d), and (f)] Hamiltonians. (a) and (b) the DOS for two "cluster-Bethe" systems containing

all rings up to order eight (dashed line) and ten (full line) respectively passing through the central atom (label 229; see Table II). (c) and (d) the DOS for two "cluster-Bethe" systems containing all rings up to order eight (dashed line) and ten (full line) respectively passing through the central atom (label 223). (e) and (f) DOS for two "cluster-Bethe" systems containing all rings up to order eight (dashed line) and ten (full line) respectively passing through the central atom (label 231). The energy is in units of V for (a), (c) and (e) and in units of eV for (b), (d) and (f).

Figure 7 Densities-of-states averaged over seventeen atoms near the center of the Polk model for two "Polk-cluster-Bethe" systems using the one-orbital [(a) and (c)] and four-orbital [(b) and (d)] Hamiltonians. (a) and (b) the DOS for a "Polk-cluster-Bethe" system with a cluster containing all rings up to order eight passing through the central atom. (c) and (d) the DOS for a "Polk-cluster-Bethe" system with a cluster containing all rings up to order ten passing through the central atom. The energy is in units of V for (a) and (c) and in units of eV for (b) and (d).

Figure 8 Densities-of-states for a "BC-8-Bethe" system with a cluster containing all rings up to order ten. The DOS was obtained using the one-orbital Hamiltonian with all interactions in the "cluster-Bethe" system equal to V (dotted line) and with interactions in the cluster equal to V and interactions in the Bethe lattice equal to $4V/\sqrt{12}$ (solid line). The energy is in units of V.

Figure 9 Densities-of-states using the one-orbital Hamiltonian for three BC-8 clusters with [(a), (c) and (e)] and without [(b), (d) and (f)] the Bethe lattice connected to the surface. (a) and (b) the DOS for a cluster containing all rings up to order six. (c) and (d) the DOS for a cluster containing all rings up to order eight. (e) and (f) the DOS for a cluster containing all rings up to order ten. The energy is in units of V and the spectra in (b), (d) and (f) have been Gaussian broadened by 0.2V.

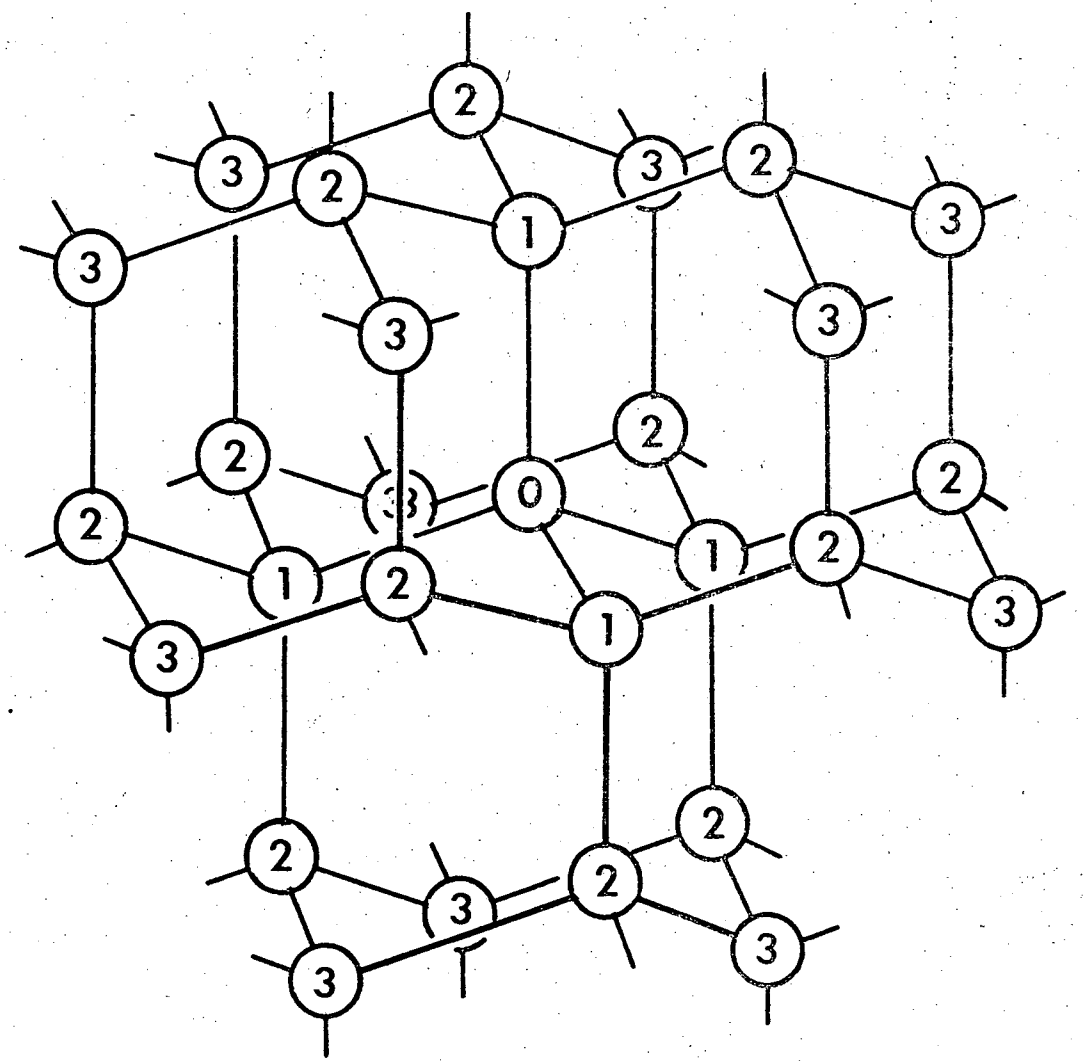

Figure 1

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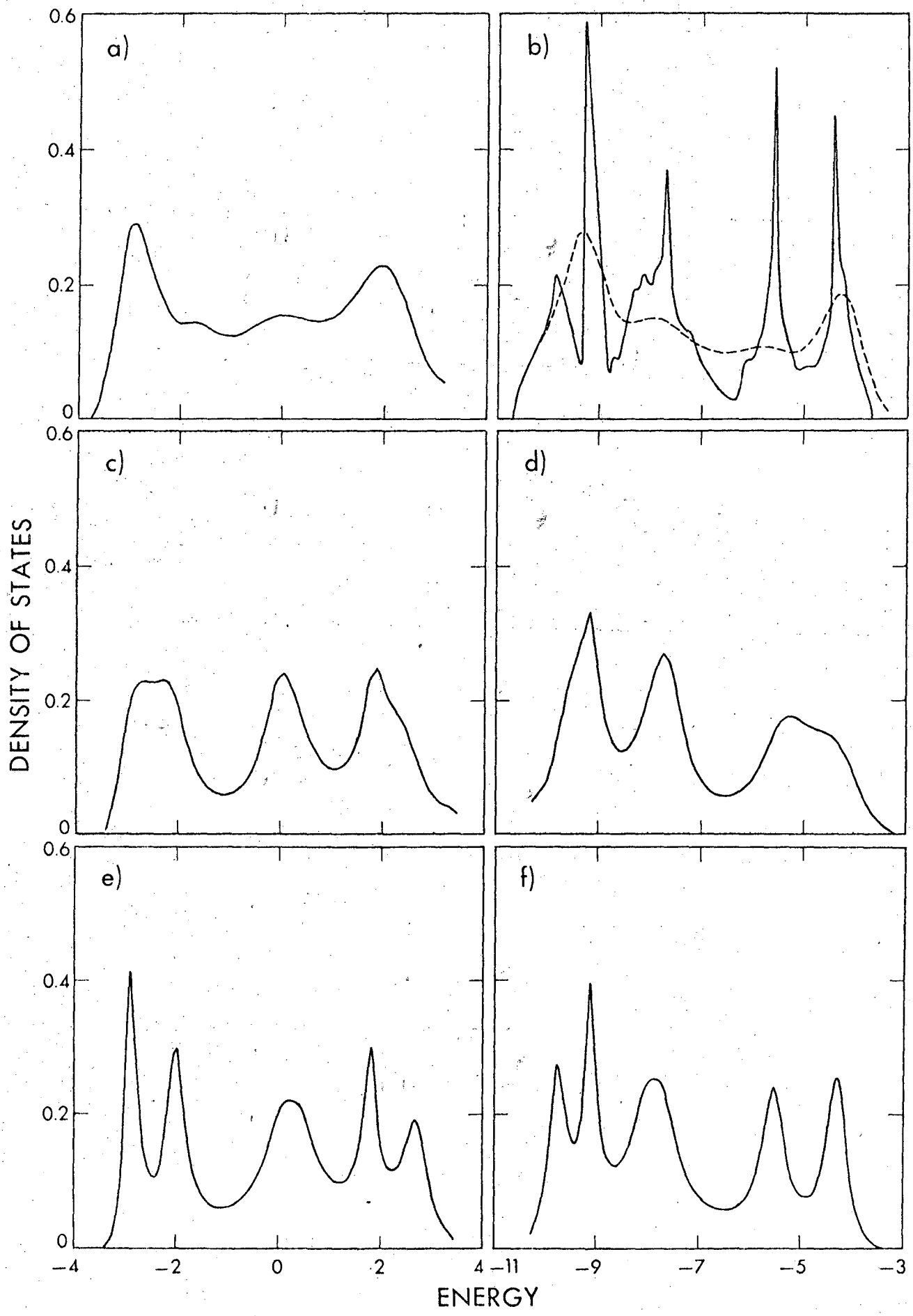

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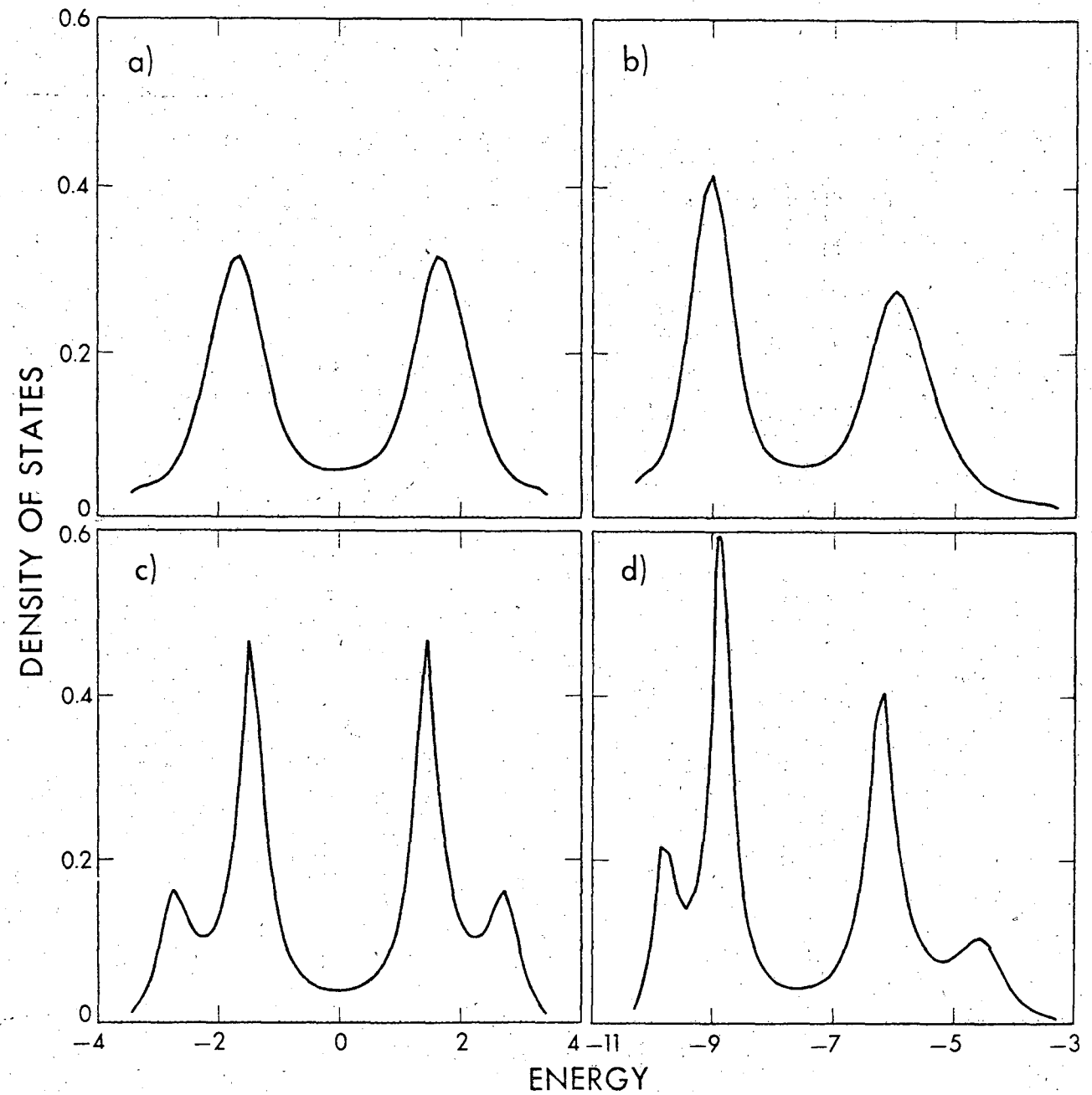

Figure 5

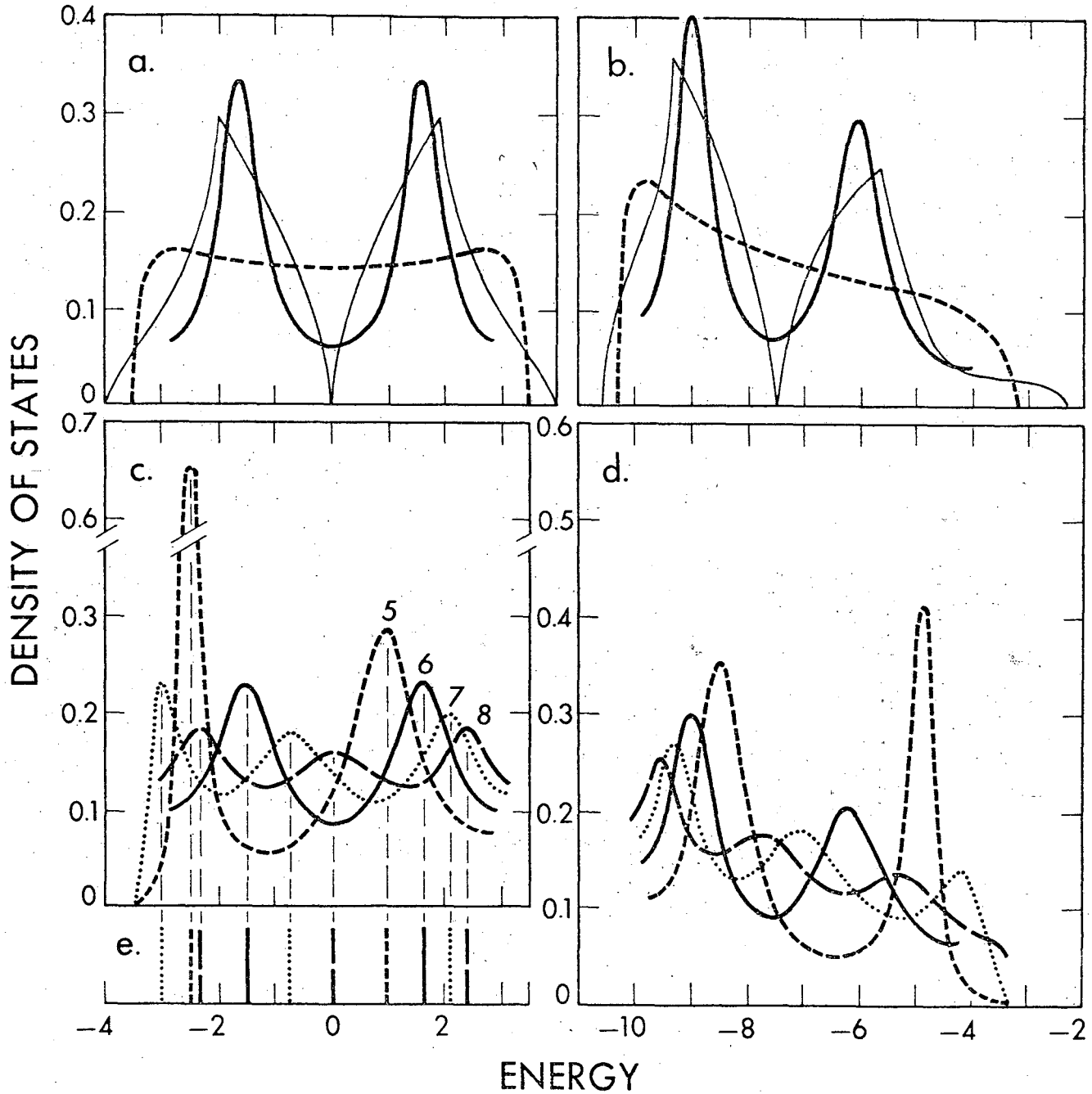

Figure 2

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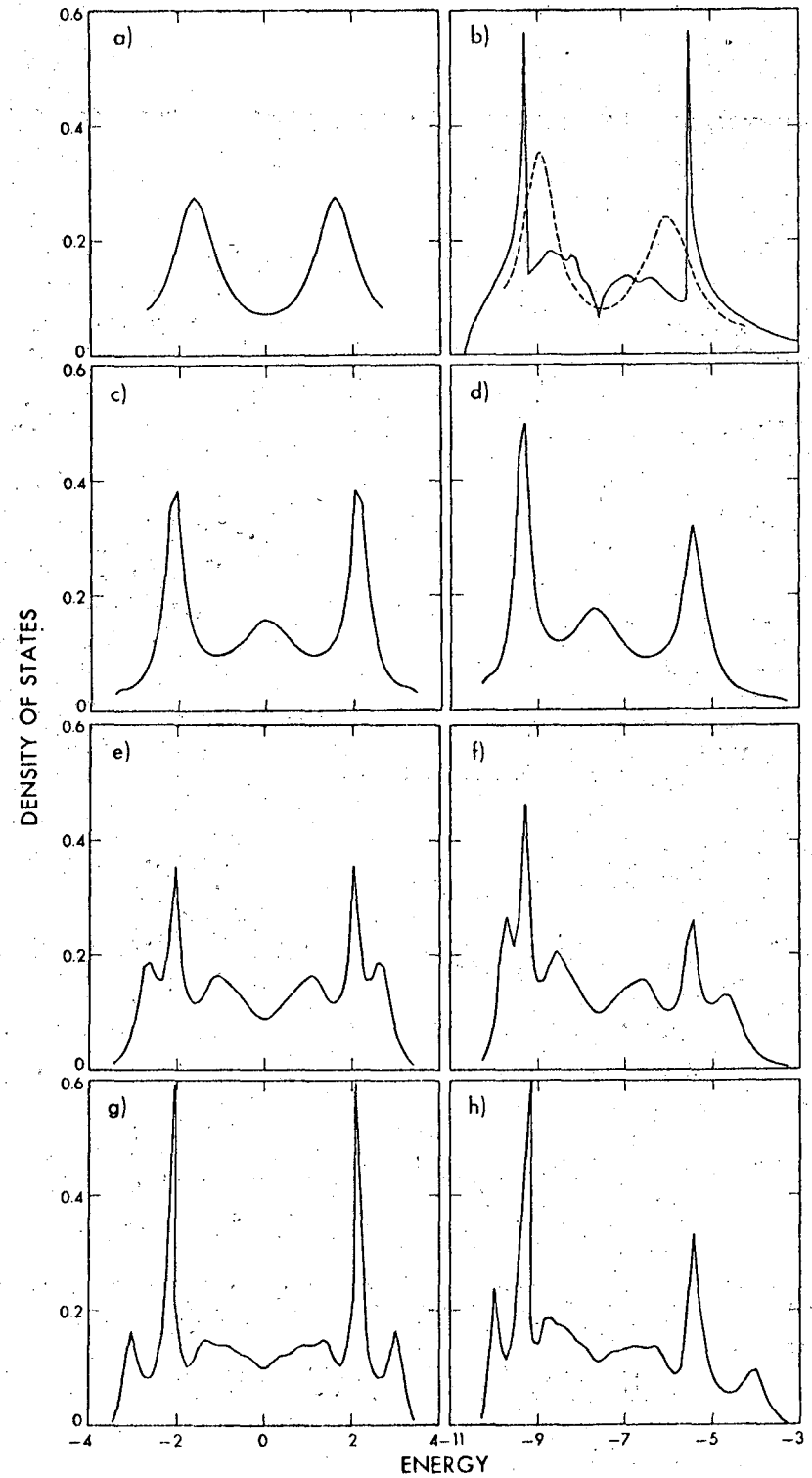

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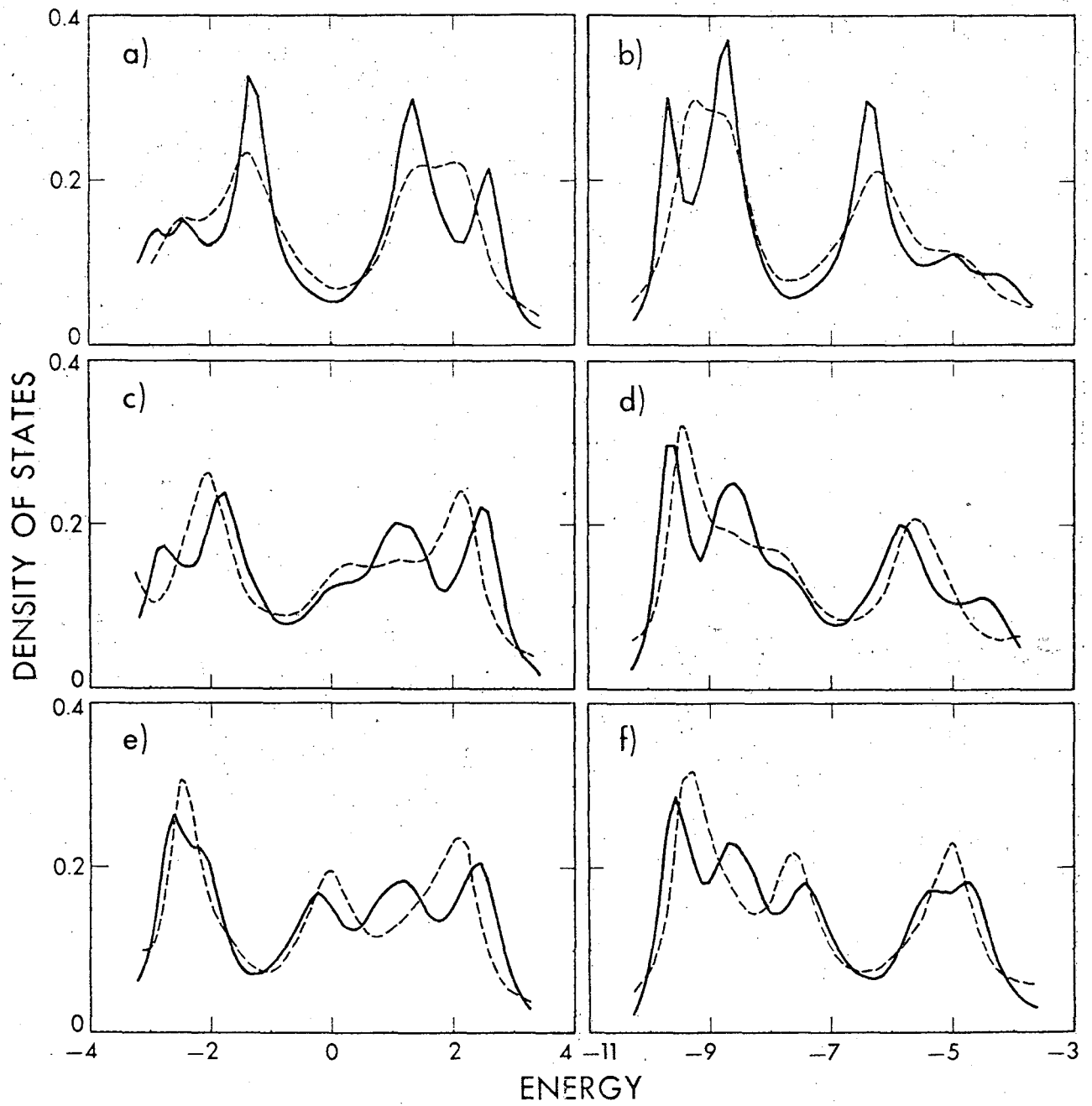

Figure 6

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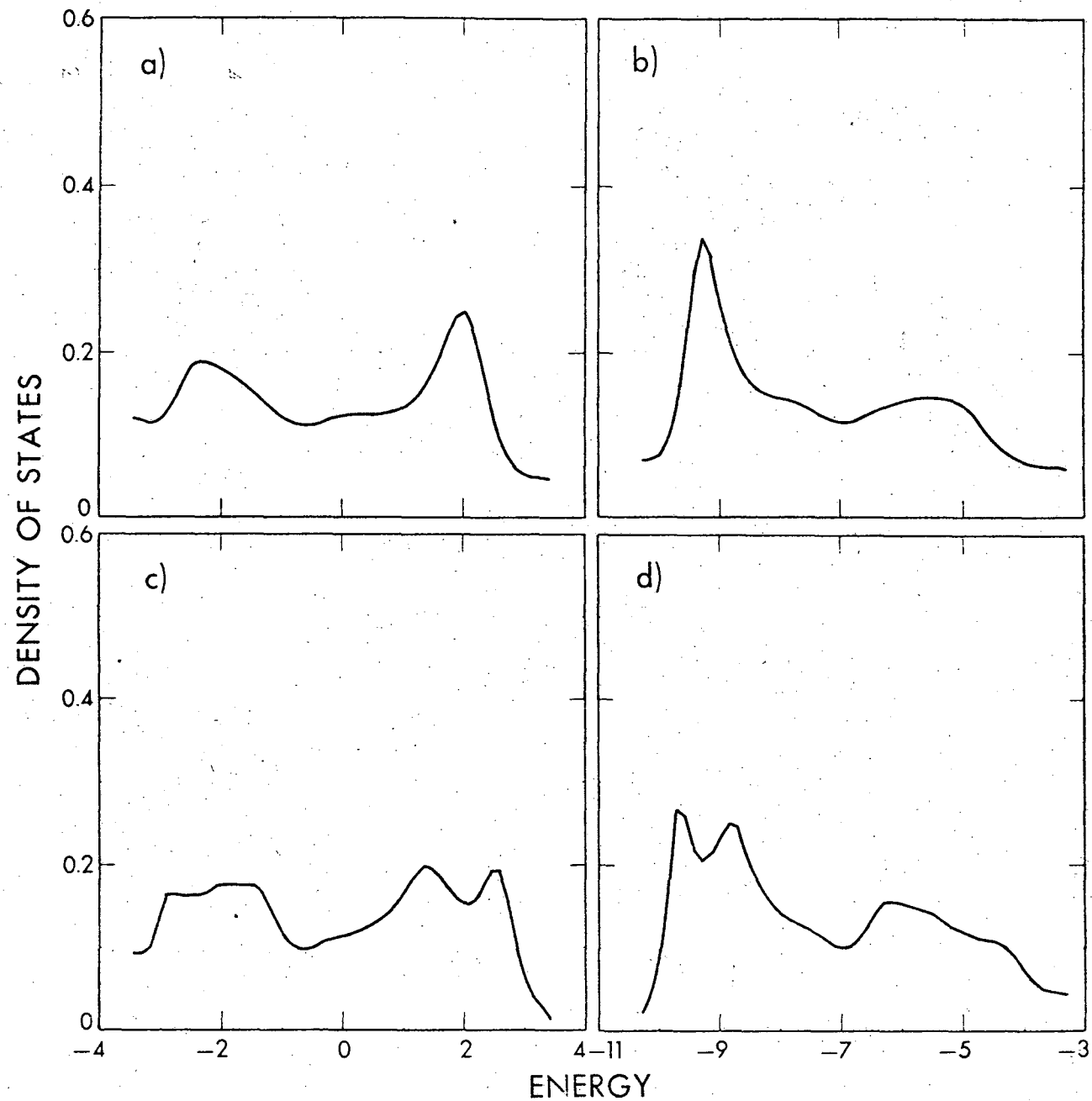

Figure 7

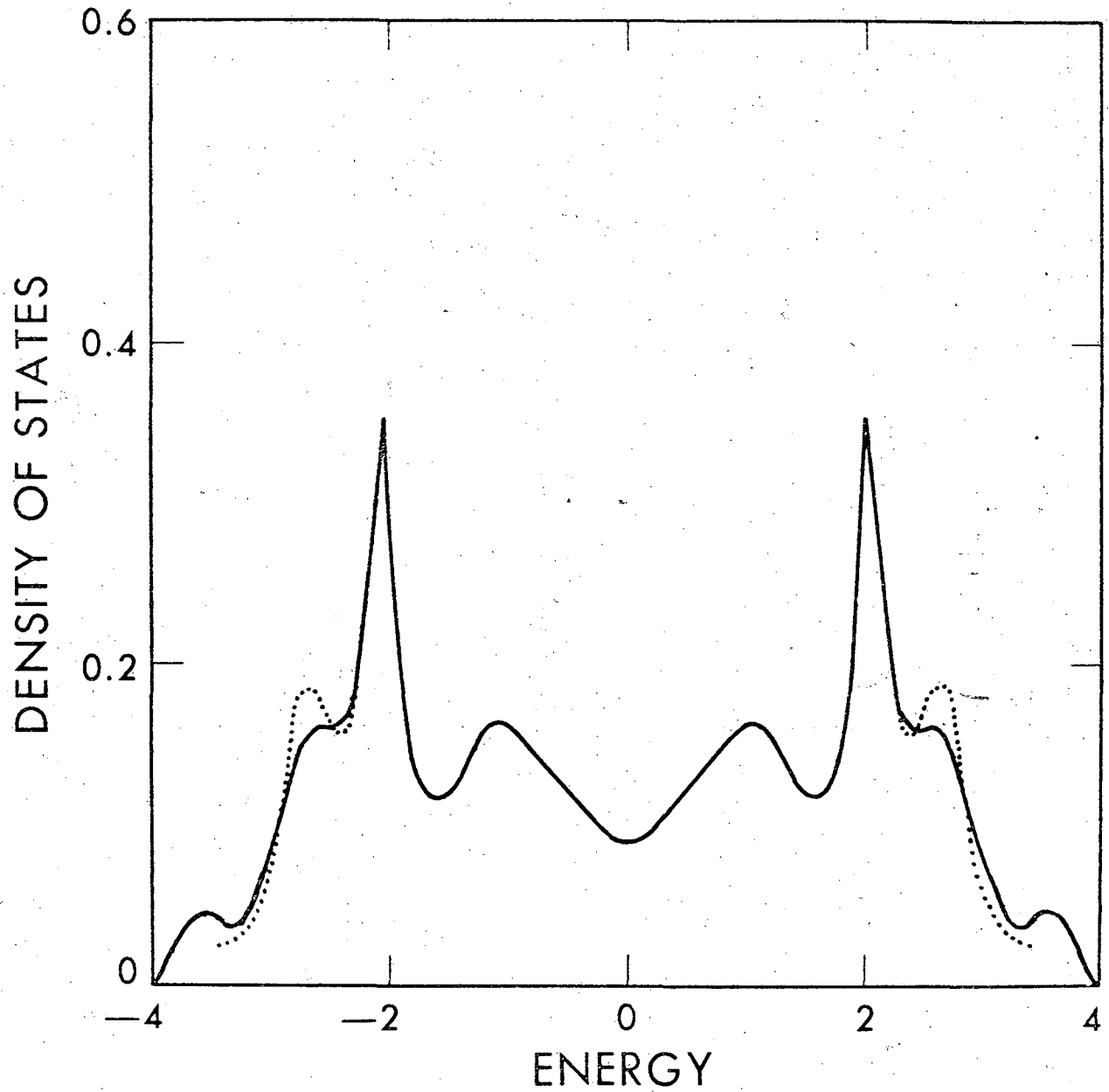

Figure 8

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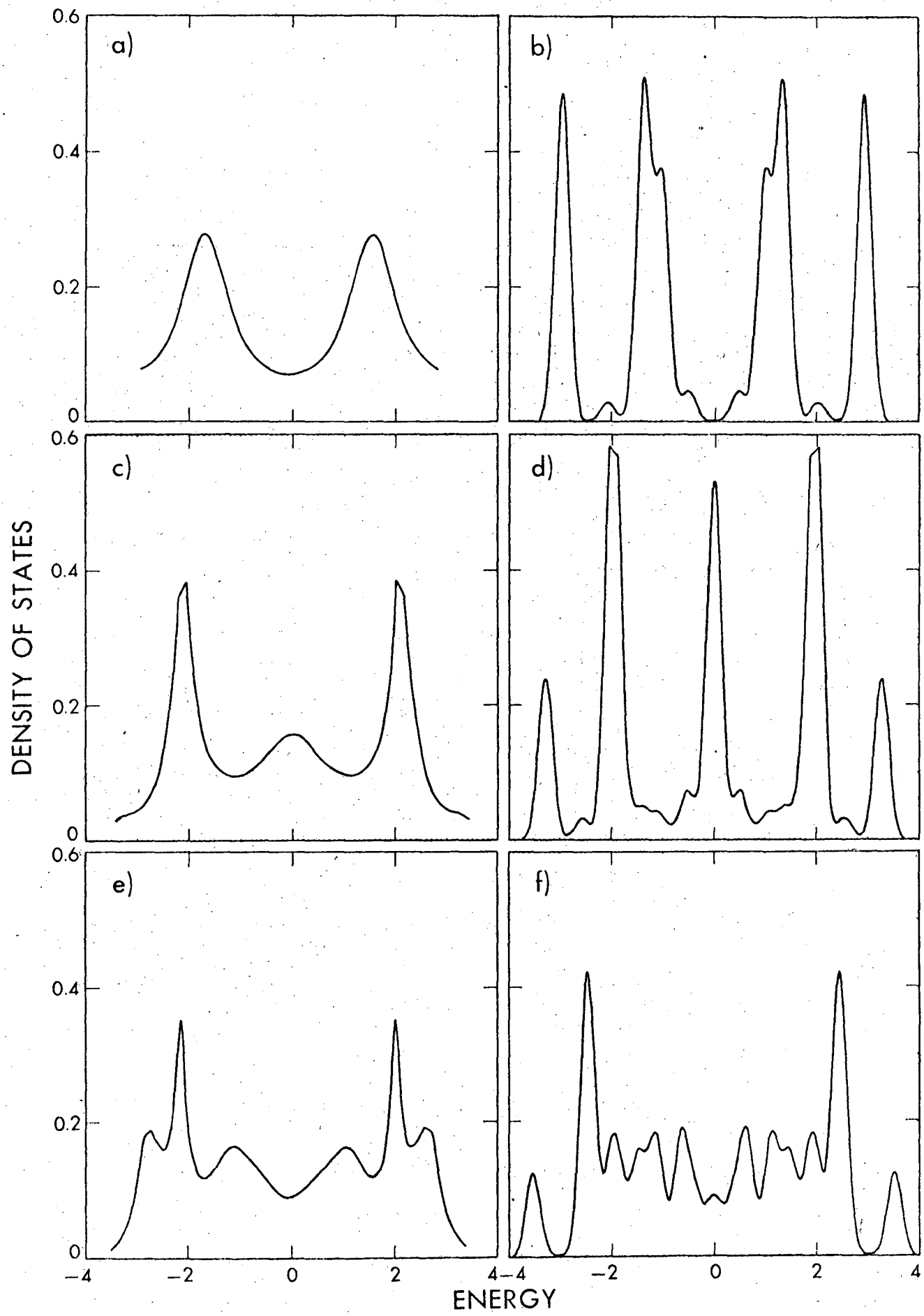

Figure 9

0 0 0 0 4 2 0 1 8 3 2

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