

appearance of the divacancy defect. The absence of the 3.9- μ band which was observed previously on the same sample and dose condition^{6,25} and identified as associated with the +1 charge state of divacancy defect, is also not understood. However, from the fact that the Fermi-level position of our neutron-irradiated Si samples is in the vicinity of the middle of the energy gap and the observation of the 1.8-, 3.3-, 3.45-, and 3.61- μ bands in all types of Si we conclude that the charge states of

divacancy defects responsible for the observation of these bands are not unique, but rather are mostly in the neutral charge state.

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Short-Range Order and Pseudogaps in Elemental Amorphous Covalent Semiconductors*

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The role of short-range order in producing a pseudogap in the density of states $\rho(E)$ of an elemental amorphous material is investigated. An approximate expression for $\rho(E)$ which emphasizes short-range order and neglects all long-range order is derived from multiple-scattering theory. This expression is used to study the influence of short-range order consisting of two atoms, a single bond, and eight atoms in the staggered and eclipsed bonding configurations on $\rho(E)$. The results of numerical calculation for amorphous sp^3 -bonded C, amorphous Si, and amorphous Ge are reported. These results suggest that the pseudogap in $\rho(E)$ may be attributed to the short-range order.

I. INTRODUCTION

Recent widespread interest in amorphous Si and

Ge has led to extensive experimental investigations of the properties of these materials.¹ One of the interesting results of these experimental investi-

gations is a clear indication that the electronic density of states participating in optical absorption^{2,3} and photoemission^{4,5} possesses a well-defined pseudogap, a range of energy where the density of states is quite small if not zero. This pseudogap is found to be similar to the band gap in the crystalline material in that it has approximately the same magnitude and separates the occupied from the unoccupied electronic states which contribute substantially to the optical absorption and photoemission.

An adequate theory of the density of states for an amorphous material has not been developed yet.⁶ The lack of long-range order in these materials^{1,7-9} precludes the direct application of the standard band-theory results which require translational invariance. However, the similarity of the short-range order in the amorphous material^{1,7,8} to that found in the perfect crystal suggests that one might use this similarity as a basis for some qualitative arguments concerning the density of states. In particular, one would expect that the structure in the electronic spectrum of the crystalline material which is determined to a large degree by the short-range order would be common to both the amorphous and crystalline material. The similarity of the pseudogap in the amorphous material to the band gap in the crystalline material suggests that the gap is one of these features. Ziman¹⁰ and Fletcher¹¹⁻¹³ have carried this argument further by suggesting that the division of the electronic states for the crystalline material into bonding and antibonding states is also applicable to the electronic states in the amorphous material. The pseudogap would then be a consequence of a gap in energy between the bonding and antibonding states as is found for the crystalline material. While this point of view is an extremely attractive one, the formalism developed by Fletcher¹¹⁻¹³ to support this idea quantitatively is subject to a number of uncertainties.¹⁴

Herman and Van Dyke¹⁵ and Brust¹⁶ have calculated the electronic spectrum of amorphous Ge by starting with a standard band-structure calculation as an initial approximation. While these calculations may produce a density of states for the amorphous material which has a pseudogap, the initial approximation of assuming long- and short-range order makes it difficult to pinpoint the role of short-range order alone.

Recently, Weaire¹⁷ has explored a simplified tight-binding model for the electronic spectrum of an amorphous material. He has been successful in showing that for an ideal random network the density of states does possess a gap. However, the rather gross simplifications involved in his model which make it possible for him to obtain rigorous results cast some legitimate doubt upon

the validity of these results for real amorphous Si and Ge.

In this paper we present the results of a study of the role of short-range order in producing a pseudogap without any assumption about the presence of long-range order.^{18,19} An approximate expression for the density of states is derived from multiple-scattering theory. This expression is used to investigate the density of states for three group-IV elements, C, Si, and Ge, with short-range order known to exist in amorphous Si and Ge.^{1,7-9} The results of this study suggest that for these materials the pseudogap is a result of the short-range order.

II. DERIVATION OF EXPRESSION FOR DENSITY OF STATES

The approximate expression for the density of states used in this paper is obtained from the multiple-scattering formalism.²⁰⁻²² This formalism in its simplest form deals with the properties of a system consisting of a number of scattering centers. The potential at each center is assumed to be spherically symmetric and these potentials are assumed to be nonoverlapping, the muffin-tin potential approximation. For a perfect crystal this formalism reduces to the standard Korringa-Kohn-Rostoker (KKR) method of calculating band structures.^{23,24}

With these assumptions about the scatters, an exact expression for the integrated density of states $N(E)$ may be derived by the following simple argument. Consider a single spherically symmetric scatter in a volume Ω . For simplicity we will assume that the potential has finite range and that this range is less than the radius of Ω . In this case, the integrated density of states $N(E)$ (the number of states per volume with energy less than E) is given by the expression^{25,26}

$$N(E) = \frac{E^{3/2}}{3\pi^2} + \frac{2}{\pi\Omega} \sum_l (2l+1)\delta_l(E), \quad (2.1)$$

where $\delta_l(E)$ is the phase shift for the l th partial wave due to the spherically symmetric scattering potential.²⁷ This expression is valid only for positive energies measured such that the potential is zero beyond the range of the scattering potential, the muffin-tin zero. The first term in Eq. (2.1) is the integrated free-particle density of states and the second term is the correction to $N(E)$ due to the scattering center and is commonly referred to as the Friedel sum. Equation (2.1) may be written in a more general form by noting that the phase shift is related to the scattering matrix²⁷ $S(E)$ by the expression

$$S_{ll'}(E) = \delta_{ll'} e^{i2\delta_l(E)}; \quad (2.2)$$

thus,

$$N(E) = \frac{E^{3/2}}{3\pi^2} + \frac{1}{\pi\Omega} \text{Im} \{ \text{Tr} [\ln(S(E))] \}. \quad (2.3)$$

The expression may be written in terms of the reaction matrix²⁷ K by simple application of the definition of K in terms of S :

$$S(E) = [1 + iK(E)][1 - iK(E)]^{-1}. \quad (2.4)$$

That is,

$$N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\Omega} \text{Im} \{ \text{Tr} [\ln(\delta_{L_1 L_2} \delta_{ij} + G_{L_1 L_2}^*(\vec{x}_i - \vec{x}_j) k_{L_2}^i(E))] \}, \quad (2.6)$$

where

$$G_{L_1 L_2}^*(\vec{R}) = -i \times \begin{cases} \sum_{L_3} 4\pi i^{l_2 + l_3 - l_1} C_{L_1 L_2 L_3} h_{L_3}^*(E^{1/2} R) Y_{L_3}(\vec{R}), & R \neq 0 \\ \delta_{L_1 L_2}, & R = 0 \end{cases} \quad (2.7)$$

and

$$C_{L_1 L_2 L_3} = \int Y_{L_1}(\Omega) Y_{L_2}(\Omega) Y_{L_3}(\Omega) d\Omega. \quad (2.8)$$

$k_i^j(E) [= \tan \delta_i^j(E)]$ is the reaction matrix for the potential at site j . This expression was originally derived by Lloyd²¹ and may be derived by the procedure outlined in Appendix B. Equation (2.6) may be rearranged so that instead of the reaction matrix for a single site the reaction matrix for a group of sites appears in Eq. (2.6). This is accomplished by introducing the concept of clusters.

The division of a disordered structure into clusters of sites proceeds according to the following procedure: We divide the material into groups of sites, and label the location of site i in group j by \vec{x}_i^j . In addition, we select a center for each group of sites and call it \vec{r}_j (for the j th group). The decomposition of the disordered structure into groups of sites is a valid decomposition into clusters if

$$|\vec{x}_i^j - \vec{r}_j| < |\vec{x}_i^k - \vec{r}_j| \quad \text{for all } i, j, k, l \text{ with } k \neq j, \quad (2.9a)$$

$$N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\Omega} \sum_j \text{Im} \{ \text{Tr} [\ln(\delta_{L_1 L_2} - iK_{L_1 L_2}(\vec{r}_j, E))] \} - \frac{2}{\pi\Omega} \text{Im} \{ \text{Tr} [\ln(\delta_{ij} \delta_{L_1 L_2} + (1 - \delta_{ij}) \pi \sum_{L_3} G_{L_1 L_3}^*(\vec{r}_i - \vec{r}_j) T_{L_3 L_2}(\vec{r}_j, E))] \}, \quad (2.11)$$

where $T_{L_3 L_2}(\vec{r}_j, E)$ is the transition matrix for cluster j . The last two terms in this expression correspond to that portion of $N(E)$ (see Appendix A) due to scattering from each cluster independently

$$N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\Omega} \text{Im} \{ \text{Tr} [\ln(1 - iK(E))] \}. \quad (2.5)$$

Equation (2.5) is valid for nonspherically symmetric scatters as well as spherically symmetric ones.²⁸ Calculation of the second term requires the reaction matrix for the object doing the scattering.

If the object doing the scattering consists of a number of scattering centers each spherically symmetric and located at position \vec{x}_i , then Eq. (2.5) may be written as²⁹

$$|\vec{r}_j - \vec{r}_k| > |\vec{r}_k - \vec{x}_i^k| \quad \text{for all } i, j, k, \text{ with } j \neq k. \quad (2.9b)$$

Criteria (2.9) require that if we draw a sphere about the center of each cluster with radius equal to the maximum distance from the center of a cluster to one of the scattering sites contained in the cluster, then this sphere must not contain the center of any other cluster or a scattering site belonging to any other cluster. For a valid decomposition of the scattering sites into clusters, Eq. (2.6) may be written as (see Appendix B)

$$N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\Omega} \text{Im} \{ \text{Tr} [\ln(\delta_{L_1 L_2} \delta_{ij} + \sum_{L_3} G_{L_1 L_3}^*(\vec{r}_i - \vec{r}_j) K_{L_3 L_2}(\vec{r}_j, E))] \}, \quad (2.10)$$

where $K_{L_3 L_2}(\vec{r}_j, E)$ is the reaction matrix for the cluster of scattering sites (see Appendix A).

Equation (2.10) can be further simplified by rearranging the last term, giving

and that portion of $N(E)$ due to scattering between clusters, respectively. Equation (2.11) is a useful expression for studying $N(E)$ for a disordered material, since it is possible to incorporate what is

known about the short-range order at least in part in the definition of the clusters.

For the disordered material, we do not have all the information to characterize the clusters precisely. Thus, a cluster could be one of a number

of different types labeled by α_i , with various orientations with respect to a fixed coordinate system β_i , and with various positions r_i . The average of Eq. (2.11) over an ensemble of various disordered solids consisting of N clusters is given by

$$N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\omega_c} \sum_{\alpha} p_{\alpha} \text{Im} \{ \text{Tr} [\ln(\delta_{L_1 L_2} - iK_{L_1 L_2}^{\alpha}(E))] \} \\ - \frac{2}{\pi\Omega} \sum_{\alpha_1 \cdots \alpha_N} \int P(\alpha_1, \vec{r}_1, \beta_1 \cdots \alpha_N, \vec{r}_N, \beta_N) d\vec{r}_1 d\beta_1 \cdots d\vec{r}_N d\beta_N \\ \times \text{Im} \{ \text{Tr} [\ln(\delta_{ij} \delta_{L_1 L_2} + (1 - \delta_{ij}) \pi \sum_{L_3} G_{L_1 L_3}^+ (\vec{r}_i - \vec{r}_j) T_{L_3 L_4}^{\alpha_j} (\beta_j, \vec{r}_j, E))] \} , \quad (2.12)$$

where p_{α} is the fraction of the clusters in the ensemble of type α , P is the probability distribution characterizing the ensemble, and $\omega_c (= \Omega/N)$ is the average volume per cluster.

The third term in Eq. (2.12) is hard to evaluate because it requires that we prescribe P for a disordered system in a realistic way and that we evaluate the determinant of an infinite matrix. Diagrammatic techniques and approximations to P^{22} could in principle be used to evaluate Eq. (2.12). However, in practice these techniques are hard to apply successfully even when simplifying approximations are made.³⁰ Other approximations might include the assumption that the ensemble over which we average for the amorphous material consists of a number of crystalline solids each made up of a single type of cluster located on a periodic lattice. The calculation of $N(E)$ for each member of the ensemble could be carried out by standard band-structure techniques and the average computed by averaging over the results for $N(E)$ for the various members of the ensemble.³¹ While these approximations would make it possible to treat the third term in Eq. (2.12), none of them correctly treats the type of correlation between clusters that one expects to find in the amorphous materials. Thus, we have chosen to neglect this term entirely in exploring the role of short-range order in producing a pseudogap and take

$$\langle N(E) \rangle = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\omega_c} \sum_{\alpha} p_{\alpha} \text{Im} \{ \text{Tr} [\ln(\delta_{L_1 L_2} - iK_{L_1 L_2}^{\alpha}(E))] \} . \quad (2.13)$$

This approximation is equivalent to calculating the integrated density of states for each different type of single cluster in a volume ω_c , and then assuming that the entire solid is made up of these independent clusters in a fraction given by p_{α} . In calculating the integrated density of states for a single cluster, the cluster is assumed to be embedded in a uniform potential whose value is given

by the muffin-tin zero for the perfect solid.

The approximation leading to Eq. (2.12) is a rather drastic one. Intuitively, we expect that as the volume of the clusters and the number of scattering centers in the cluster increase, the value of $\langle N(E) \rangle$ given by Eq. (2.12) will approach the value for the infinite solid. At worst this convergence should go as the surface-to-volume ratio of the cluster. However, in this paper the clusters used consist of at most eight atoms, and in a sense all of the atoms are near the surface. Furthermore, this approximation not only neglects all long-range order (which gives the relative position and relative orientation of clusters separated by a large distance), but also neglects certain correlations in the location and orientation of nearby clusters which are part of the short-range order. On the other hand, some of the short-range order potentially lost by this approximation is retained by taking into account the effect of nearby clusters upon the single-site potentials (see Sec. III). In the disordered solid the phase of the scattered wave from the various portions of the solid is randomized by the disorder, leading to a partial cancellation of the contribution due to multiple scattering between clusters.

For our purposes in this paper, this approximation is convenient since it makes possible a study of short-range order in producing a pseudogap without attempting to make some uncontrolled estimate of the last term. It also seems unlikely that this approximation will invalidate the results shown here. An evaluation of the neglected term should enhance the pseudogap behavior of the density of states shown by the approximate calculations.

The expression for the density of states $\rho(E)$ is obtained simply by differentiating Eq. (2.12) with respect to energy:

$$\rho(E) = \frac{E^{1/2}}{2\pi^2} - \frac{2}{\pi\omega_c} \sum_{\alpha} p_{\alpha} \frac{d}{dE} \text{Im} \{ \text{Tr} [\ln(\delta_{L_1 L_2} - iK_{L_1 L_2}^{\alpha}(E))] \} . \quad (2.14)$$

While the equations derived are strictly valid for energies above the muffin-tin zero, the energies of interest for this paper, the equations for $\rho(E)$ and $N(E)$ can be modified for use for energies below the muffin-tin zero by dropping the free-particle contribution which is zero and letting $E^{1/2} = i(|E|)^{1/2}$. However, in this case the $\rho(E)$ would consist of a series of δ functions corresponding to the bound states of the cluster.

III. SHORT-RANGE ORDER AND SINGLE-SITE SCATTERING PROPERTIES

To study the density of states for an amorphous material by evaluating Eq. (2.14), we must specify the spatial configuration of atoms in the clusters and the scattering properties of each atom in the cluster.

The spatial configuration of atoms in clusters is determined by the short-range order found in the amorphous material. While detailed information about the exact structure of amorphous Si and Ge is not available, the radial distribution functions obtained by x-ray and electron-diffraction techniques^{1,7-9} indicate the existence of short-range order extending to the second nearest neighbor. On the average, each atom is surrounded by four nearest neighbors with an average nearest-neighbor distance which deviates by only a few percent of the value for the perfect crystal. A peak is found in the radial distribution function at second-nearest-neighbor distance for the perfect crystal. Using this information, Grigorovici and Manaila⁸ and Polk³² have constructed random network models for amorphous Si and Ge. The model constructed by Grigorovici and Manaila divides quite naturally into eight-atom clusters in the staggered bonding configuration which is found in the diamond lattice and in the eclipsed bonding configuration which along with the staggered configuration is found in the wurzite lattice⁸ (see Fig. 1). The model constructed by Polk contains not only the two bonding configurations but also all intermediate rotations of the three atoms at the top with respect to the three atoms at the bottom. However, the difference between the staggered and eclipsed bonding configurations still gives the largest variation of bonding configurations found in the amorphous material. Hence, we have selected these clusters with an interatomic spacing given by that found in the perfect crystal as the basis for our calculation. This choice allows us to adequately describe the type of short-range order found in the amorphous material as well as its deviation from the perfect crystal. For comparison, we have also made calculations for clusters consisting of one atom and two atoms with the crystal-line interatomic spacing.

The single-site scattering properties of the atoms in the amorphous material should be obtained by

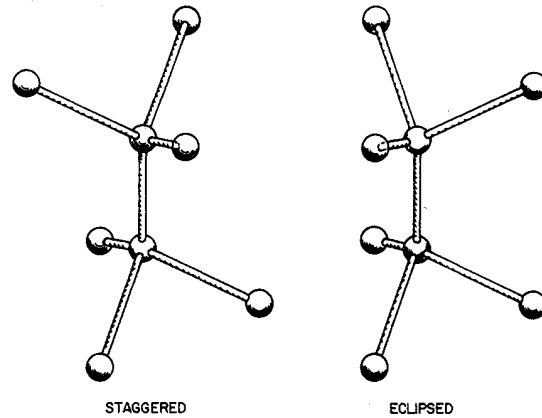


FIG. 1. Clusters of eight atoms in the staggered and eclipsed configurations.

making a muffin-tin approximation to the potential about each scattering center and then solving the scattering problem for this potential. The fluctuations in the spatial arrangement of the near neighbors of a site lead to variation in the potential about the various sites. Hence, we would expect that a slightly different muffin-tin potential and scattering properties would be required for each site. However, the existence of well-defined spatial arrangements of nearest neighbors in the amorphous material which are like the spatial arrangements found in the perfect crystal suggests that we approximate all of the single-site scattering properties of atoms in the amorphous material by the scattering properties for atoms in the perfect crystal.

The muffin-tin potential used in computing these scattering properties was constructed according to the procedure given by Mertens.³³ The potential at each site was taken to be the Hartree-Fock-Slater potential for the ground state of the atoms given by Herman and Skillman.³⁴ Modifications of the atomic potential due to the nearest-neighbor atoms in the perfect crystal were computed according to the expression

$$V_{\text{crystal}}(r) = V_{\text{atomic}}(r) + V_{\text{atomic}}(a - r), \quad (3.1)$$

where a is the interatomic spacing. The radius of the muffin tin was taken to be one-half the interatomic spacing. The value of the muffin-tin zero calculated by averaging the potential in the crystal external to the muffin tins was taken from Ref. 33. Single-site phase shifts for this potential were obtained by numerical integration of the radial Schrödinger equation. In the case of Si and Ge, the s -phase shifts were scaled by a factor of 1.054 and 1.07, respectively. This scaling brings the calculated band structure into semiquantitative agree-

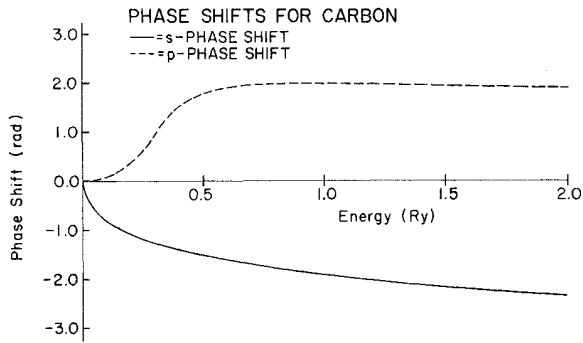


FIG. 2. Phase shifts for C as a function of energy.

ment with the accepted band structures.^{35,36} This solved some of the difficulties associated with the application of the KKR method of calculating band structure for these materials.³³

The phase shifts obtained by this procedure are shown in Figs. 2-4. These figures indicate the rather strong similarity of *s*- and *p*-phase shifts for all of these materials. In particular, the weak resonance in the *p*-phase shift is an important feature. The *s*- and *p*-phase shift alone were sufficient to give an adequate band structure for diamond, but for Si and Ge it was necessary to include the *d*-phase shift.

The band structures obtained from these phase shifts are shown in Figs. 5-7.³³ While all of these band structures suffer from the inexactness inherent in the application of the muffin-tin approximation to the potential in a diamond lattice, these results indicate that the electronic spectra are adequately described for the points to be made in this paper.

IV. NUMERICAL RESULTS FOR DENSITY OF STATES

Using the parameters and structures detailed in Sec. III, Eq. (2.14) has been evaluated numerically to give the density of states. Since the region of the pseudogap occurs at energies greater than the muffin-tin zero, only energies greater than the

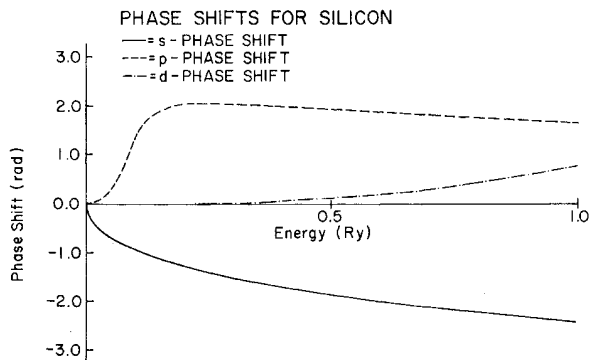


FIG. 3. Phase shifts for Si as a function of energy.

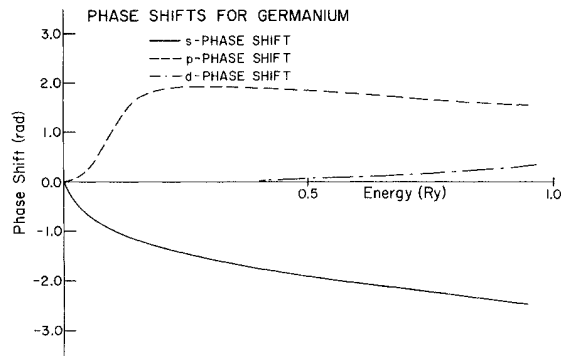


FIG. 4. Phase shifts for Ge as a function of energy.

muffin-tin zero were explored. To make clear the role of various types of clusters in a density of states, we first evaluate Eq. (2.14) for clusters of one type. That is, we take $p_\alpha = 1$, where α is the type of cluster under consideration, and $p_{\alpha'} = 0$ for $\alpha' \neq \alpha$.

The results of these calculations for C are shown in Figs. 8 and 9. Figure 8 shows the variation in $\rho(E)$ for clusters with differing numbers of atoms. For one site, the principal structure in $\rho(E)$ consists of a single peak at approximately 0.3 Ry, which is due to the weak resonance in the *p*-phase shift. $\rho(E)$ for clusters of two atoms has two principal features: two peaks in the range 0-0.5 Ry which are the result of splitting the single peak in $\rho(E)$ for one site, and a rather small peak at higher energies at about 1.3 Ry. For eight-site clusters, $\rho(E)$ has structure similar to that found

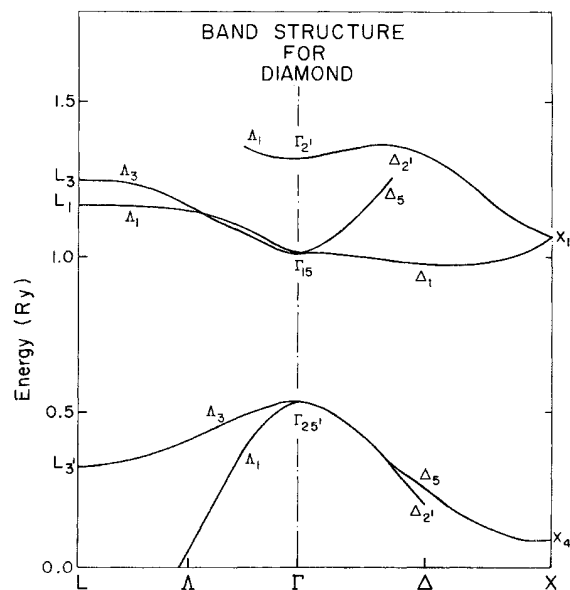


FIG. 5. Band structure for diamond.

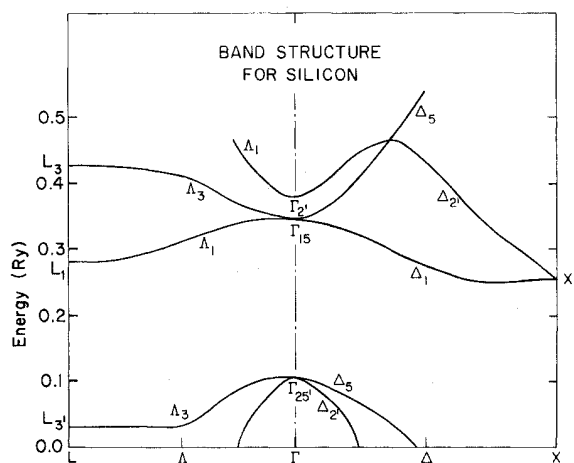


FIG. 6. Band structure for Si.

in the two-site cluster; however, the valley separating peaks between 0–0.5 Ry and the peak at 1.3 Ry is better defined, owing to an increase in the magnitude of the peak at approximately 1.35 Ry, a decrease in $\rho(E)$ in the range 0.5–1.0 Ry, and an increase in the sharpness of the edges of the peaks bordering the valley.

Figure 9 shows the results for the eight-center clusters with the staggered or eclipsed configurations as well as the free-particle density of states [the first term in Eq. (2.14)]. Several points should be noted from these results. First, $\rho(E)$ for the staggered and eclipsed structures are qualitatively similar. Second, $\rho(E)$ in the valley region is below that due to the free-particle term only, indicating a partial cancellation of the free-particle density of states in that range of energies. Finally, comparison of the location of the valley in $\rho(E)$ with the location of the band gap in the perfect crystal (between $\Gamma_{25'}$ and Δ_1^m shown on the abscissa of Fig. 9) shows that they occur in approximately the same energy range.

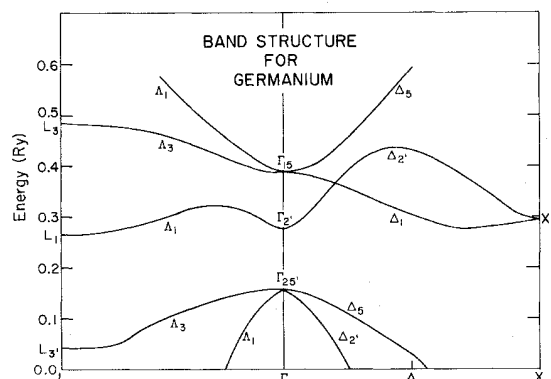


FIG. 7. Band structure for Ge.

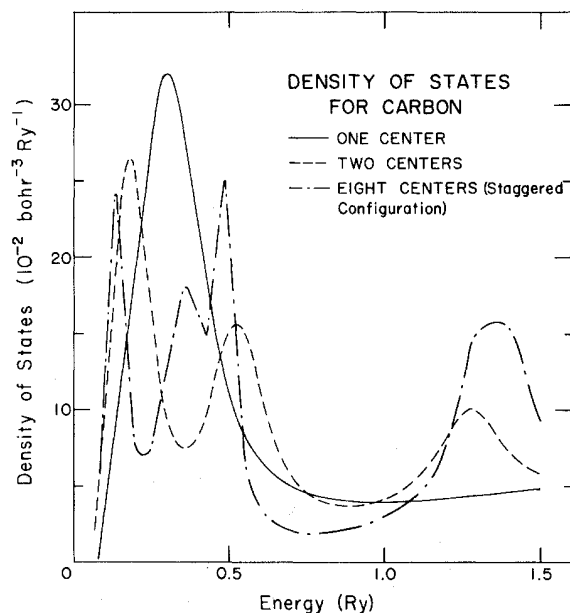


FIG. 8. Density of states for clusters of one, two, and eight C sites as a function of energy.

The amorphous material will contain both the staggered and eclipsed configurations of eight-atom clusters as well as fluctuations about these configurations. Thus, $\rho(E)$ for the disordered material would be obtained by substituting suitable values of p_α in Eq. (2.14). For example, the results for $\rho(E)$ for half staggered and half eclipsed are shown in Fig. 10. This $\rho(E)$ possesses features which are consistent with the density of states

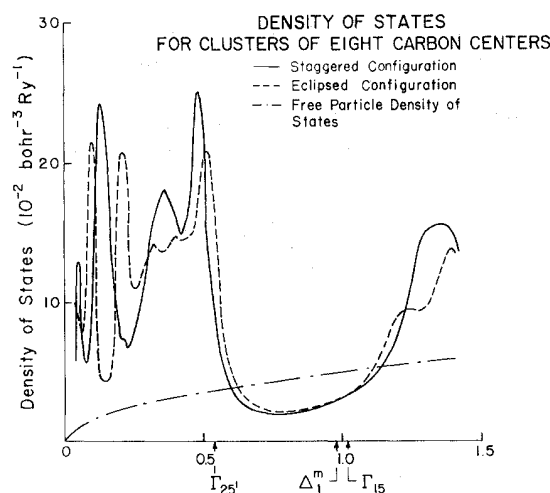


FIG. 9. Density of states for clusters of eight C sites in staggered and eclipsed configurations and the free-particle density of states as a function of energy. The locations of the relevant energy levels in the band structure are shown along the energy axis.

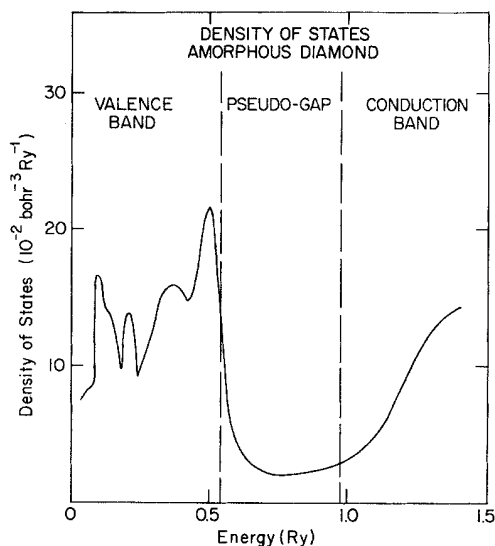


FIG. 10. Hypothetical density of states for "amorphous diamond" obtained by averaging with equal weight the results for the staggered and eclipsed configurations.

suggested by optical^{2,3} and photoemission^{4,5} experiments. The range of energies at low energy giving a high density of states is identified with the "valence band," and the range of energies at high energy giving a high density of states is identified with the "conduction band." These two bands are separated by a region of low density of states, the

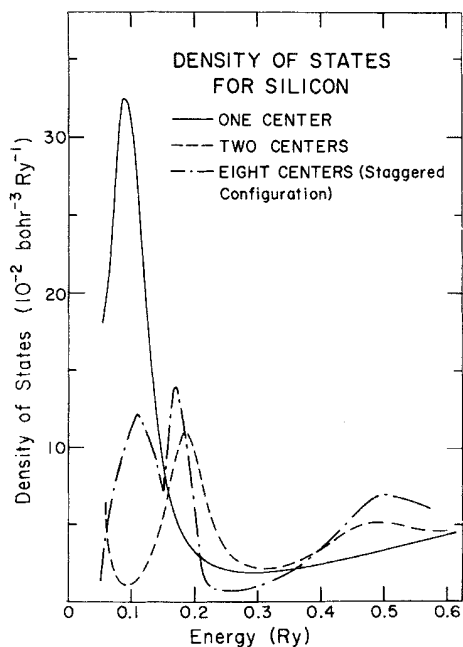


FIG. 11. Density of states for clusters of one, two, and eight Si sites as a function of energy.

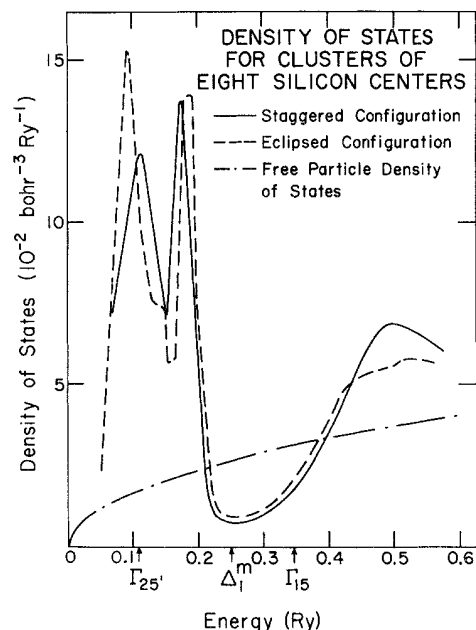


FIG. 12. Density of states for clusters of eight Si sites in the staggered and eclipsed configurations and the free-particle density of states as a function of energy. The locations of the relevant energy levels in the band structure are shown along the energy axis.

pseudogap. This pseudogap has a width which is similar to the band gap found in the perfect crystal. The process of averaging tends to smooth out

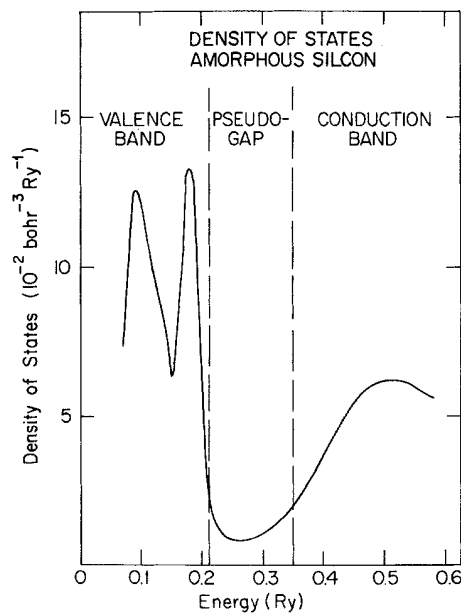


FIG. 13. Hypothetical density of states for "amorphous Si" obtained by averaging with equal weight the results for the staggered and eclipsed configurations.

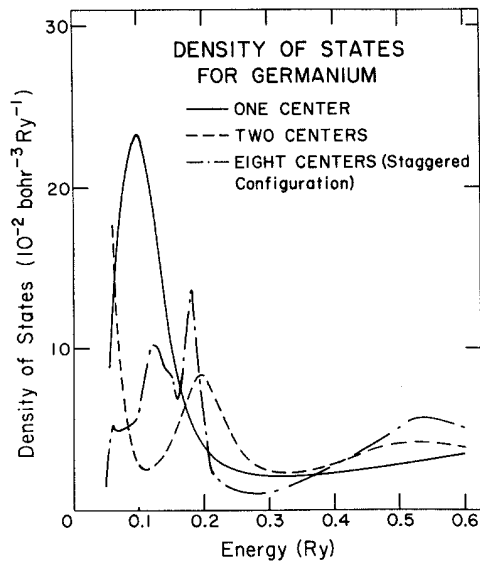


FIG. 14. Density of states for clusters of one, two, and eight Ge sites as a function of energy.

the structure in the curves of Fig. 9 in the "valence band" and "conduction band." Inclusion of other clusters whose spatial configuration is intermediate to the staggered and eclipsed configurations plus fluctuations about these configurations will smooth out more of the structure in the valence

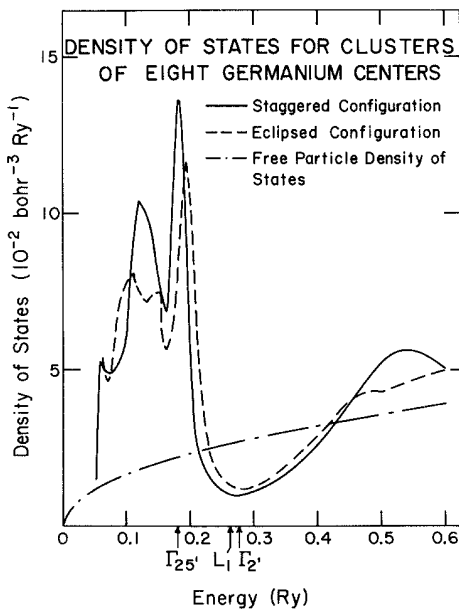


FIG. 15. Density of states for clusters of eight Ge sites in the staggered and eclipsed configurations and the free-particle density of states as a function of energy. The location of the relevant energy levels in the band structure is shown along the energy axis.

band and conduction band. However, the similarity of $\rho(E)$ for the various clusters in the region about the pseudogap strongly suggests that the feature would not be lost by any averaging over clusters similar to those used for the calculations shown in Fig. 9.

Similar results were obtained for Si and Ge as shown in Figs. 11–16. In these cases the variation of $\rho(E)$, in going from one- to two- to eight-site clusters, is similar to that found for C, and again the difference between the staggered and eclipsed configurations is small in the pseudogap region. However, the results for Si and Ge do differ in one way from those for C, that is, in the location of the valley in $\rho(E)$ with respect to the band gap in the perfect solid. The band gap in the perfect solid occurs at lower energy in both of these materials than that found for the valley in the density of states for the clusters. This difference in location can be traced to the addition of the d -phase shift in the single-site scattering properties, which not only adjusts the band structure slightly but also moves the gap to lower energies. The addition of the d -phase shift does not noticeably shift the structure in $\rho(E)$. In fact, an s - p calculation for Si and Ge does give a band gap which occurs at energies more closely associated with the valley in $\rho(E)$; however, the band structure obtained in this calculation is not in as good a qualitative agreement with the accepted band structure as the s - p - d band structure.

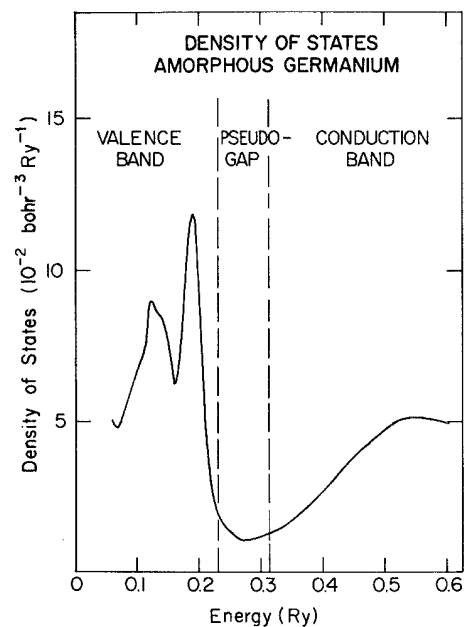


FIG. 16. Hypothetical density of states for amorphous Ge obtained by averaging with equal weight the results for the staggered and eclipsed configurations.

V. DISCUSSION OF RESULTS AND CONCLUSION

The principal result of these calculations is to show that the short-range order in amorphous Si and Ge is capable of giving a pseudogap in the density of states. This pseudogap may be viewed as the result of the scattering properties of the cluster. For energies in the valence and conduction bands, the cluster scatters in a resonant fashion, leading to a high density of states in much the same way the d resonance leads to a large density of states in the transition metals. On the other hand, in the pseudogap, the clusters scatter in an anti-resonance fashion, leading to a low density of states. When these clusters are placed in the solid, the valence and conduction bands result from the resonantlike "states" for the cluster. The pseudogap is a direct consequence of the cluster tending to "repel" electrons in this energy range. The filling of space with the clusters effectively gives the electron little place to go. Consequently, we obtain a pseudogap.

These scattering properties of the cluster are the results of both the single-site scattering properties and the spatial location of the atoms in the cluster. Since the p -phase shift is the only phase shift with a resonance behavior, and since the p resonance plays an important role in determining the location of the $\Gamma_{25'}$ and Γ_{15} ^{37,38} states which are at the top of the valence band and near the bottom of the conduction band in the perfect crystal, one might suspect that it is responsible for the structure found in the density of states. However, calculations of the density of states for clusters of more than one site with either the s - or the p -phase shift set equal to zero produced results which are qualitatively different from those reported here. This result indicates that both the s - and p -phase shifts play a role in producing the scattering properties necessary to produce a pseudogap.

The minimum value of the density of states in the pseudogap region obtained from these calculations cannot be taken as a reliable estimate of the depth of the pseudogap in the amorphous material. The minimum obtained here is four orders of magnitude higher than the upper bound that Donovan, Spicer, and Bennett² have assigned on the basis of the optical absorption in amorphous Ge. This discrepancy is not unexpected when one realizes that a precise zero for the density of states would require an exact cancellation of the free-particle part by the terms that we have approximated. Thus, the value of the minimum of the density of states is particularly sensitive to an approximation such as the one that has been made here. Determination of the value of the density of states in the pseudogap and of the sharpness of the edges near the pseudogap requires a better treatment of

the scattering between clusters.

The correlations of the pseudogap found in these calculations with the magnitude and location of the band gap in the perfect crystal suggest that one might attribute the gap in the perfect solid in part to the short-range order and the scattering properties of the clusters of atoms in the staggered configuration. The role of the translational invariance in producing details of the density of states could in part be assessed by comparing the density of states from an approximate calculation of this nature with the density of states for a full band-structure calculation on the same material.

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APPENDIX A: DERIVATION OF EXPRESSIONS FOR REACTION AND TRANSITION MATRICES FOR A NUMBER OF SCATTERERS

In this appendix we derive an expression for the reaction matrix in the angular momentum representation of a group of scattering centers satisfying the standard muffin-tin approximation. These results have been derived in an essentially equivalent way by Lloyd²⁸ and are reported here merely for completeness.

For definiteness, we introduce a coordinate system and label the location of the j th scattering center by \vec{x}_j . The potential at each scattering center will be assumed to be nonzero only over a sphere of radius a . The standard muffin-tin approximation is made for the potentials.

To obtain an expression for the reaction matrix, we need the solution to the Schrödinger equation at energy $E = \kappa^2$ which behaves as²⁷

$$\psi(r) = j_{l_1}(\kappa r) Y_{L_1}(r) - \sum_L K_{L_2 L_1} n_{L_2}(\kappa r) Y_{L_2}(r) \quad (\text{A1})$$

for $r > |\vec{x}_j| + a$ for all j . Once the solution given by Eq. (A1) is obtained, it is easy to identify the reaction matrix. Equation (A1) can be obtained by application of Green's theorem:

$$\psi(\vec{r}) = \int_s d\vec{s} \cdot [\psi(\vec{r}') \nabla' G^p(\vec{r}, \vec{r}') - G^p(\vec{r}, \vec{r}') \nabla' \psi(\vec{r}')] , \quad (\text{A2})$$

where

$$G^p(\vec{r}, \vec{r}') = - \frac{\cos \kappa |\vec{r} - \vec{r}'|}{4\pi |\vec{r} - \vec{r}'|} = \sum_L \kappa j_l(\kappa r <)$$

$$\times n_i(\kappa r_s) Y_L(\vec{r}) Y_L(\vec{r})$$

and κ is the smaller of $|\vec{r}|$ and $|\vec{r}'|$, and κ is the larger of $|\vec{r}|$ and $|\vec{r}'|$. The surface S is a large sphere at ∞ , and the surfaces of spheres surrounding each one of the scattering centers with radius slightly larger than the range of the potential a . Using Eq. (A1) to compute the integral over the sphere at infinity, we have

$$\begin{aligned} \psi(\vec{r}) = & j_i(\kappa r) Y_L(\vec{r}) + \int d\vec{S} \cdot [\psi(\vec{r}') \nabla' G^p(\vec{r}, \vec{r}') \\ & - G^p(\vec{r}, \vec{r}') \nabla' \psi(\vec{r}')], \end{aligned} \quad (\text{A3})$$

where S_s denotes the surfaces of the spheres surrounding the scattering sites. Since the solution of the Schrödinger equation on a sphere about scattering center i with radius greater than a can be taken to be of the form²⁷

$$\begin{aligned} \sum_{L_2} A_{L_2 L_1}^i [j_{L_2}(\kappa |\vec{r} - \vec{x}_i|) - k_{L_2}^i(E) \\ \times n_{i_1}(\kappa |\vec{r} - \vec{x}_i|)] Y_{L_1}(\vec{r} - \vec{x}_i), \end{aligned} \quad (\text{A4})$$

where $A_{L_2 L_1}^i$ are constants which are to be determined, the second term in Eq. (A3) can be evaluated directly, yielding on comparison with Eq. (A1)

$$K_{L_1 L_2} = \sum_{i L_3} \Delta_{L_1 L_3}(\vec{x}_i) k_{L_3}^i(E) A_{L_3 L_2}^i, \quad (\text{A5})$$

where

$$\Delta_{L_1 L_2}(\vec{x}) = \sum_{L_3} 4\pi i^{l_3+1} j_{l_3}(\kappa x) Y_{L_3}(\vec{x}) C_{L_1 L_2 L_3}, \quad (\text{A6})$$

where $C_{L_1 L_2 L_3}$ is defined in Eq. (2.8). Thus, the evaluation of the K matrix reduces to obtaining the set of constants $A_{L_2 L_1}^i$. To do this we again apply Green's theorem in the region of one of the scattering spheres and require that the solution in that region be of the form given in Eq. (A4). This yields a set of equations for the $A_{L_2 L_1}^i$,

$$A_{L_2 L_1}^i = \Delta_{L_1 L_2}(\vec{x}_i) - \sum_{j L_3} G_{L_2 L_3}^p(\vec{x}_i - \vec{x}_j) k_{L_3}^j(E) A_{L_3 L_1}^j, \quad (\text{A7})$$

where

$$G_{L_1 L_2}^p(\vec{R}) = \begin{cases} \sum_{L_3} 4\pi i^{l_3+1} j_{l_3}(\kappa R) \sum_{L_3} (\vec{R}), & R \neq 0 \\ 0, & R = 0. \end{cases} \quad (\text{A8})$$

Solving these equations and substituting the solution into Eq. (A5), we obtain

$$K_{L_1 L_2} = \sum_{i L_3, j L_4} \Delta_{L_1 L_3}(\vec{x}_i) k_{L_3}^i(E) (M^{-1})_{L_3 i; L_4 j} \Delta_{L_4 L_2}(-\vec{x}_j), \quad (\text{A9})$$

where M is a matrix with elements

$$M_{L_3 i; L_4 j} = \delta_{ij} \delta_{L_3 L_4} + G_{L_3 L_4}^p(\vec{x}_i - \vec{x}_j) k_{L_4}^j(E). \quad (\text{A10})$$

The transition matrix T is obtained from the definition of the T matrix in terms of the K matrix²⁷:

$$T = -\pi^{-1} K(1 - iK)^{-1}. \quad (\text{A11})$$

APPENDIX B: DERIVATION OF EXPRESSION FOR INTEGRATED DENSITY OF STATES

The derivation of the expression for the integrated density of states (2.10) follows very simply once it is noted that all the operations in Appendix A used to derive the reaction matrix are still valid if the group of single-site scattering centers is replaced by a group of valid clusters as defined in Sec. II. In this case the reaction matrix \bar{K} for the group of clusters is given in terms of the reactions matrices for the clusters $K(r_i, E)$ by the expression

$$\begin{aligned} K_{L_1 L_2} = \sum_{i L_3, j L_4, L_5} \Delta_{L_1 L_3}(\vec{r}_i) K_{L_3 L_4}(\vec{r}_i, E) \\ \times M_{L_4 i; L_5 j}^{-1} \Delta_{L_5 L_2}(-\vec{r}_j), \end{aligned} \quad (\text{B1})$$

where M is now the matrix with elements

$$M_{L_3 i; L_4 j} = \delta_{ij} \delta_{L_3 L_4} + \sum_{L_5} G_{L_3 L_5}^p(\vec{r}_i - \vec{r}_j) K_{L_5 L_4}(\vec{r}_j, E)$$

and \vec{r}_i refers to the center of the cluster as discussed in Sec. II.

To facilitate the algebraic manipulations to follow, it is convenient to write Eq. (B1) in an abbreviated algebraic form,

$$\bar{K} = \Delta_1 K M^{-1} \Delta_2. \quad (\text{B2})$$

Substitution of Eq. (B2) into Eq. (2.5) yields

$$N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\Omega} \text{Im} \{ \text{Tr}[\ln(1 - i\Delta_1 K M^{-1} \Delta_2)] \}.$$

Using the identity

$$\text{Tr}[\ln(1 - iAB)] = \text{Tr}[\ln(1 - iBA)],$$

we have that

$$N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\Omega} \text{Im} \{ \text{Tr}[\ln(1 - i\Delta_2 \Delta_1 K M^{-1})] \}. \quad (\text{B3})$$

But one can show from the definition of Eq. (A6) that Δ satisfies the identity²⁸

$$\Delta_{L_1 L_2}(\vec{R}_1 + \vec{R}_2) = \sum_{L_3} \Delta_{L_1 L_3}(\vec{R}_1) \Delta_{L_3 L_2}(\vec{R}_2). \quad (\text{B4})$$

Thus, the product of $\Delta_2 \Delta_1$ in Eq. (B3) may be replaced by a single Δ , Δ_3 , whose argument is the difference between the location of two clusters. Further, one can remove the matrix inverse M from Eq. (B3) to obtain

$$\begin{aligned} N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\Omega} \text{Im} \{ \text{Tr}[\ln(M - i\Delta_3 K)] \} \\ + \frac{2}{\pi} \text{Im} \{ \text{Tr}[\ln(M)] \}. \end{aligned} \quad (\text{B5})$$

However, M is in general a real matrix. Thus, the last term in Eq. (B5) is zero. Restoring the indices to the matrices, we have that

$$N(E) = \frac{E^{3/2}}{3\pi^2} - \frac{2}{\pi\Omega} \text{Im} \{ \text{Tr} [\ln(\delta_{ij} \delta_{L_1 L_2})$$

$$+ \sum_{L_3} G_{L_1 L_3}^+(\vec{r}_i - \vec{r}_j) K_{L_3 L_2}(\vec{r}_j, E) \} \}, \quad (\text{B6})$$

where $G_{L_1 L_2}^+$ is defined by Eq. (2.7). This is the desired result.

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$$Y_L(\Omega) = \left(\frac{(2+1)(l-|m|)!}{2\pi(l+|m|)!} \right)^{1/2} P_l^{|m|}(\cos\theta) \times \begin{cases} \cos m\phi, & m > 0 \\ 1/\sqrt{2}, & m = 0 \\ \sin |m|\phi, & m < 0. \end{cases}$$

The index L denotes the doublet (l, m) .

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