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Correlated diagonal and off-diagonal disorder in amorphous solids

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A self-consistent self-energy approximation is developed to study effects of fluctuations in site energies and transfer matrix elements in tight-binding models of disordered solids. Correlations between energies for adjacent sites, and between site energies and transfer amplitudes to neighbor sites, are included explicitly. The latter are shown to produce asymmetries in the energy spectrum, while the former have effects similar to those of uncorrelated diagonal and off-diagonal fluctuations with altered variances.

I. INTRODUCTION

Electron energy eigenstates in many disordered solids can be described in terms of a tight-binding Hamiltonian which includes "diagonal" terms representing the various energies of localized (e.g., Wannier) electron wave functions at the sites of the solid, and "off-diagonal" terms representing the different transition matrix element associated with electron transfer between neigboring sites. The energy spectrum for such a system is then the set of eigenvalues of a very large, sparse matrix whose nonzero elements are random, though not necessarily independent, variables. The present work studies the estimation of the eigenvalue distribution (or density of states) when correlations among matrix elements, both diagonal and off-diagonal, associated with neighboring sites may be important. An effective-medium approximation is developed which incorporates such correlations in a natural and self-consistent fashion, and the use of the method is demonstrated for systems in which fluctuations of each site energy are correlated with fluctuations in the transfer matrix elements coupling the site to its neighbors.

This application of the general technique can be compared with the calculations of John and Schreiber,[1] and more recently Klafter and Jortner,[2] who treat a model in which diagonal matrix elements are correlated with off-diagonal elements which have a Lorentzian or Cauchy distribution. Except for features associated with the unphysically large tails of Lorentzians, the results found here confirm the main qualitative features of previous calculations—in particular a pronounced asymmetry produced by correlations between diagonal and off-diagonal disorder.

It is worth noting that in many real amorphous materials, it is reasonable to expect that structural irregularities will produce fluctuations in off-diagonal matrix elements which are likely to dominate variations in site energies. Moreover, the same variations in local geometry which change off-diagonal terms from their average value also are responsible for variations in site energies, thus significant correlations of diagonal with off-diagonal fluctuations are to be expected.

To model a solid in which geometrical disorder leads to both topological and local quantitative variations, one can consider a lattice of N sites, without translational symmetry, but with uniform coordination (each site has the same number n of immediate neighbors), described by the so-called "adjacency matrix," defined explicitly below, which specifies which sites are neighbors of which other sites. The structure should have long-range homogeneity and isotropy, which means essentially that matrix elements of sufficiently high powers of the adjacency matrix should be site-independent. The topology of the lattice itself influences the energy spectrum in important ways, including the rounding of the Van Hove discontinuities of periodic structures and the introduction of asymmetries associated with changes in ring statistics.[3] The interest here, however, is on the effects of matrix element within a given structure. One then can consider ensemble averages, for a fixed topology, over values of the random diagonal and off-diagonal Hamiltonian matrix elements

The effective-medium approximation developed here differs from the widely used coherent-potential approximation (CPA) in the criterion for the choice of values of the energy-dependent parameters which serve as the uniform diagonal and off-diagonal elements in an equivalent effective Hamiltonian. Yonezawa and Odagaki[4] have discussed the extension of the CPA, originally developed for the treatment of systems with independent diagonal disorder, to systems decomposable into a set of independent homomorphic units or clusters. More recently, Kaplan *et al.*[5] have shown how to extend the calculation of conditionally averaged Green's functions (useful for the treatment of substitutional defects, as in alloys) to include self-consistently scatterings from clusters of various sizes. This method, like the CPA of Yonezawa *et al.*, provides the correct analytic properties of Green's functions for any amount of disorder. However, it cannot in its present form deal with correlations among fluctuations except for those uniquely specified by which species of ions are present at the involved sites. The CPA criterion for parameters of an equivalent effective medium is that the average of the single-cluster scattering matrix vanish. This approach can deal satisfactorily with correlated fluctuations only if they occur within a single cluster. Instead, the approach presented here identifies a self-consistent self-energy which incorporates (to all orders in a perturbation expansion) the contributions of double scatterings by any pair of correlated fluctuations. The resulting Green's functions can have unphysical analytic properties for large enough amounts of disorder, but are acceptable for quite large fluctuations, such as those to be expected in a real material with a reasonably stable structure.

II. THE SELF-CONSISTENT SELF-ENERGY

The tight-binding Hamiltonian is represented by the matrix $\mathscr{H}_{ij}=a_i\delta_{ij}+b_{ij}\mathscr{N}_{ij}$, where the indices i and j label sites. The adjacency matrix $\mathscr{N}_{ij}$ has elements 1 when i and j are nearest neighbors and zero otherwise; it thus specifies the topological structure of the atomic array. The site energies a_i and transfer matrix element b_{ij} are random (but perhaps correlated) variables. The goal is to approximate the ensemble average of the resolvent operator $(z1-\mathscr{H})^{-1}$ as a function of the complex energy variable z. A formal perturbation expansion for the resolvent results if the Hamiltonian is separated into fixed and fluctuating parts:

$$\begin{aligned}\mathscr{H}&=H+V\ ,\\ H_{ij}&=a\delta_{ij}+b\mathscr{N}_{ij}\ ,\\ V_{ij}&=e_i\delta_{ij}+v_{ij}\mathscr{N}_{ij}\ .\end{aligned}\tag{1}$$

a and b are taken to be the average values of a_i and b_{ij}, respectively, so that the random e_i and v_{ij} have zero expectation values. Neglecting V completely would thus be the so-called "virtual crystal approximation." A self-energy operator is defined by

$$\langle (z1-\mathscr{H})^{-1}\rangle=(z1-\mathscr{H}-\Sigma)^{-1}\ .\tag{2}$$

A diagrammatic representation of the perturbation series for Σ includes only linked diagrams. A self-consistent approximation to Σ is obtained by taking

$$\Sigma_s=\langle VG_sV\rangle\ ,\tag{3a}$$

which involves the corresponding approximate average resolvent

$$G_s=(z1-\mathscr{H}-\Sigma_s)^{-1}\ .\tag{3b}$$

This approximation, or its equivalent, has been used with good results for a number of different problems.[6] In diagrammatic terms, it amounts to a summation of "nested diagrams." For the present calculation it has two important features. First, it allows inclusion of correlations among the different random terms in V. Second, however, when correlations exist only over short distances between sites, Σ_s will have nonzero matrix elements only between nearby sites. In particular, suppose the only nonvanishing expectation values of products of two elements of V are the following:

$$\begin{aligned}&\langle v_{ij}^2\rangle=\alpha\ ,\\ &\langle e_ie_j\rangle=\beta_1\ \text{ for } i=j\\ &=\beta_2\ \text{ for } i \text{ and } j\\ &\text{ nearest neigbors}\\ &\langle e_iv_{ij}\rangle=\gamma\ .\end{aligned}\tag{4}$$

Then a direct evaluation of Σ_s yields only a diagonal element $(\beta_1+n\alpha)G_0+2n\gamma G_1$ and nearest-neighbor elements

$$2\gamma G_0+(\beta_2+\alpha)G_1\ .$$

The new quantities are averaged elements of G_s, defined by

$$\begin{aligned}G_0&=N^{-1}\mathrm{Tr}G_s\ ,\\ G_1&=(nN)^{-1}\mathrm{Tr}\mathscr{N}G_s\ .\end{aligned}\tag{5}$$

It follows that G_s has a form equivalent to a renormalization of $\mathscr{H}$:

$$G_s=(z'1-b'\mathscr{N})^{-1}\ ,\tag{6}$$

with renormalized parameters

$$z'=z-a-(\beta_1+n\alpha)G_0-2n\gamma G_1 \, ,$$
$$b'=b+(\beta_2+\alpha)G_1+2\gamma G_0 \, . \tag{7}$$

These are self-consistency relations, since G_0 and G_1 on the right-hand sides of the equations are functions of z' and b' through Eq. (6).

The functional form of G_0 is determined by the eigenvalue spectrum of $\mathcal{N}$. The eigenvalues are real and bounded by $\pm n$. A convenient spectral representation may be introduced by denoting the eigenvalues of $\mathcal{N}$ by $nx_i, -1<x_i<1$, and defining a density of eigenvalues by

$$f(x)=\frac{1}{N}\sum_i \delta(x-x_i) \, . \tag{8}$$

It can be seen that $f(x)$ is simply the density of states in the absence of disorder, with energy units chosen so that a, the energy at the band center, is zero, and the total bandwidth is 2. It is normalized so that its integral over all x is unity.

The representation of G_0 then has the simple form

$$G_0=\int \frac{f(x)dx}{z'-nb'x} \, . \tag{9}$$

It is also useful to note that

$$z'G_s-b'\mathcal{N}G_s=1 \, , \tag{10}$$

from which G_1 can be expressed as

$$G_1=(z'G_0-1)/nb' \, . \tag{11}$$

For specific applications of this technique, then, one selects an appropriate $f(x)$, specifies values of the disorder parameters $\alpha,\beta_1,\beta_2,\gamma$, and solves Eqs. (7), (9), and (11). An approximate density of states is then given by

$$g(E)=-\frac{1}{\pi}\lim_{\epsilon\to 0+}\operatorname{Im}G_0(E+i\epsilon) \, . \tag{12}$$

The results for some particular examples are presented in the following section.

III. SOME SPECIFIC EXAMPLES

It is convenient to rewrite the equations to be solved as follows. Dimensionless variables are defined by

$$Z=z'/nb \, ,$$
$$E=z/nb \, , \tag{13}$$
$$F=b'/b \, .$$

Energy units are chosen as described above; i.e., $a=0$ and $b=1$. Then Eqs. (7) become

$$Z=E-c_1G_0-c_2G_1 \, ,$$
$$F=1+c_2G_0+c_3G_1 \, . \tag{14}$$

The three parameters measuring the disorder are

$$c_1=\beta_1+\alpha n \, ,$$
$$c_2=2\gamma n \, , \tag{15}$$
$$c_3=(\alpha+\beta_2)n \, .$$

In order to explore the consequences of correlations among Hamiltonian matrix-element fluctuations, a generalization of the model studied by John and Schrieber[1] and Klafter and Jortner[2] can be used. The off-diagonal fluctuations v_{ij} are taken to be independent identically distributed random variables with zero mean and variance $\langle v^2\rangle$. For the diagonal fluctuations, take

$$e_i=\delta_i+A\sum_j \mathcal{N}_{ij}v_{ij} \, , \tag{16}$$

where the quantities δ_i are independent random variables with zero mean and variance $\langle\delta^2\rangle$. A is any real constant, and when nonzero, produces correlations between adjacent diagonal fluctuations as well as between diagonal and off-diagonal elements. The coefficients c_i are then given by

$$c_3=(1+A^2)\langle v^2\rangle/nb^2 \, ,$$
$$c_1=c_3+\langle\delta^2\rangle/n^2b^2 \, , \tag{17}$$
$$c_2=2A\langle v^2\rangle/nb^2 \, .$$

Before a discussion of general features, it may be useful to consider some numerical results. The first examples use the spectrum for a linear chain, only because the effects of varying disorder parameters are easily seen in the sharp peaks of the density of states. For this topology $n=2$, and the Green's functions are

$$G_0(Z,F)=(Z^2-F^2)^{-1/2} \, ,$$
$$G_1=(ZG_0-1)/F \, . \tag{18}$$

Equations (14) and (18) may be solved iteratively. For an initial choice of Z and F, Eqs. (18) give G_0 and G_1, which can be inserted in Eqs. (14) to give a new pair Z,F. This straightforward approach converges quite rapidly for reasonable amounts of disorder except very close to the band edges, where alternative numerical techniques may be used to speed convergence.

Figure 1 shows the density of states when

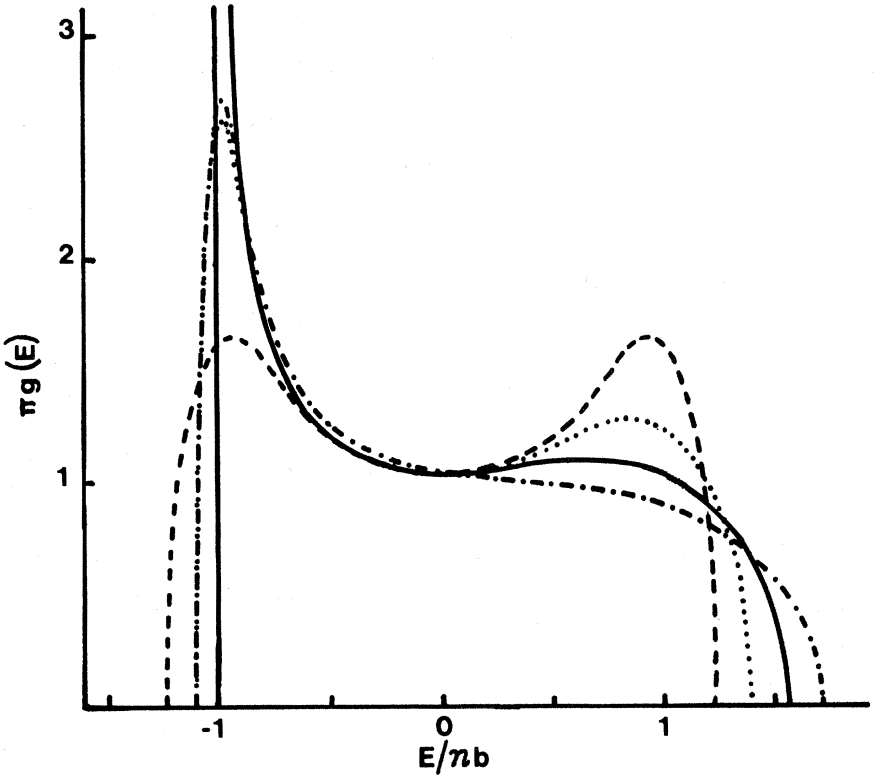

FIG. 1. Linear-chain density of states vs energy for fixed off-diagonal disorder and varying correlation, the diagonal disorder being due entirely to the correlations. Values of the correlation parameter A (see text) are: — — — $A=0$, · · · $A=0.5$, —— $A=1.0$, —·—·—· $A=1.5$.

$\langle\delta^2\rangle=0$, with $\langle v^2\rangle=0.04nb^2$, which corresponds to an rms variation in the off-diagonal Hamiltonian matrix elements of ~28% of their mean. Results are shown for values of $A=0$, 0.5, 1, and 1.5. This corresponds to the earlier work in which all the diagonal disorder is induced by the correlations between diagonal and off-diagonal fluctuations. The results are in qualitative agreement with the features found previously. In addition to rounding of the peaks and broadening of the band, there is a strong asymmetry about the band center.

When $\langle v^2\rangle$ and $\langle\delta^2\rangle$ are held constant and A is varied, the size of the diagonal energy fluctuations changes at the same time that the amount of correlation does, so that both effects are present together in the results of Fig. 1. Alternatively, the mean-square flucuations of both diagonal matrix elements may be held fixed as the amount of correlation is varied, by changing $\langle\delta^2\rangle$ together with A. Changes in the density of states for different amount of correlation, with the variances of the diagonal and off-diagonal matrix elements held fixed in this way, are shown in Fig. 2. The same value for $\langle v^2\rangle$ as for Fig. 1 is used, and the diagonal fluctuations chosen so that $\langle\delta^2\rangle=0$ when $A=1.5$.

It can be seen that the total band width is determined primarily by the widths of the diagonal and off-diagonal matrix element distributions and is quite insensitive to the varying degree of correlation. The asymmetry, however, clearly reflects the correlation. Figures 1 and 2 also show that values of A greater than unity present no problem, in contrast with the Lloyd-type model of the earlier studies.

As a final example, Fig. 3 shows the same general features for the density of states in the three-dimensional diamond lattice. Here the coordination number is four, and the Green's function replacing Eq. (18) can be written in terms of complete elliptic integrals.[7–9] The explicit formulas and their numerical evaluation are discussed in the Appendix. The parameter values of Fig. 3 correspond to the same fractional spread in transfer matrix elements of ~28%. The two disordered spectra are for the same fluctuations of the diagonal and off-diagonal elements, but with no correlation ($A=0$) in one case and $A=1$ in the other.

It can be seen that the same fractional variation

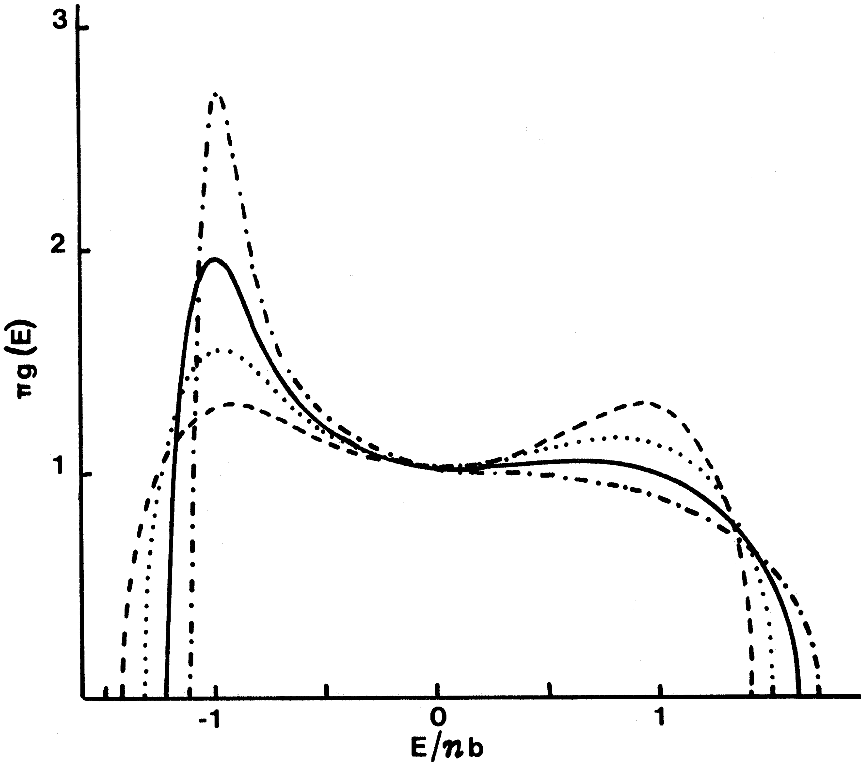

FIG. 2. Linear-chain density of states for fixed diagonal and off-diagonal order but varying correlation. Correlation parameter values are the same as in Fig. 1.

in matrix elements produces a smaller fractional change in bandwidth, which is simply a consequence of the higher coordination. The qualitative effects of broadening and asymmetry are the same for this lattice, however, and would be found in the spectrum for any other topology.

IV. DISCUSSION

In addition to permitting the explicit evaluation of electronic energies incorporating the consequences of correlated disorder, this calculation provides direct insights into the nature of spectrum changes from different types of disorder, through the form of the self-consistent renormalization relations of Eqs. (7), which involve the parameters α_1, α_2, β, and γ measuring the size and correlations of Hamiltonian matrix element fluctuations.

Asymmetry of the spectral bands is due directly, and solely, to the parameter γ, the correlation between flucuations in site energies and transfer amplitudes to neighboring sites. To make this explicit, it is useful to rewrite the spectral representations in terms of the function

$$D(\omega)=\int \frac{f(x)dx}{1-x/\omega} ,$$

where $\omega=z'/b'$. Then the relevant Green's functions take the form

$$G_0(z',b')=D(\omega)/z' ,$$

$$G_1(z',b')=[D(\omega)-1]/b' .$$

When the unperturbed spectrum is symmetric, $f(x)=f(-x)$, then so is $D(\omega)=D(-\omega)$. Also $D(\omega)$ is an analytic function of ω off the real axis, so that $D(-\omega^*)=D^*(\omega)$.

Now consider the behavior of the relations

$$z'=z-(\beta_2+n\alpha)G_0-2n\gamma G_1 ,$$

$$b'=b+(\beta_2+\alpha)G_1+2\gamma G_0 , \tag{7'}$$

under the mapping $z\to -z^*$ and $b\to b^*$. From the symmetry of $D(\omega)$, we also have $G_0\to -G_0^*$ and $G_1\to G_1^*$. The equations are changed only in the sign preceding γ in each. Thus the self-consistent spectrum is symmetric if and only if $\gamma=0$.

It may be noted that a sign change in γ simply reflects the spectrum about the band center, so that only positive values of the parameter A needed

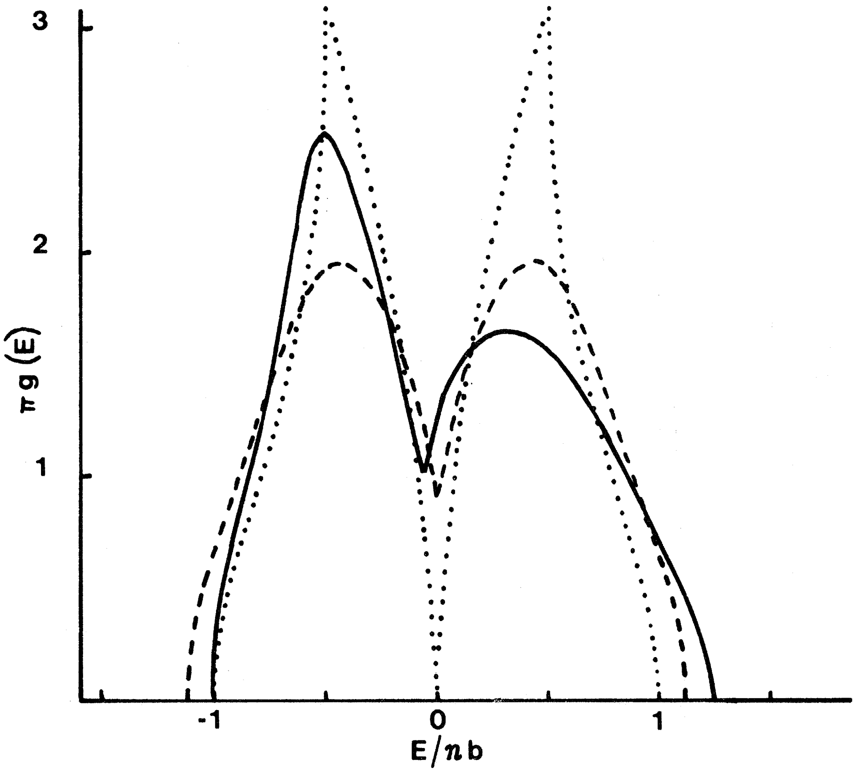

FIG. 3. Diamond lattice density of states for fixed diagonal and off-diagonal disorder but different correlations. — — — $A=0$, —— $A=1$, · · · state density with no disorder.

consideration in the preceding section. Also, the induced asymmetry does not shift the mean eigenvalue. This is simply a consequence of the choice of the "unperturbed" Hamiltonian as that for the virtual crystal approximation, with all fluctuations having identically zero mean values. In fact, since the self-energy is exact through second order in the fluctuations, the spectral moments through the second are exact.

Useful insights are also provided concerning the effects of other correlations. From Eqs. (7) it can be seen directly that positive (or negative) correlations between site energies on neighboring sites, parameterized by β_2, have the same effect as a decrease (increase) in the variance of off-diagonal fluctuations, parametrized by α, together with an increase (decrease) in the single-site energy variance β_1.

The self-energy approximation developed here can be extended in a straightforward manner to include additional types of correlation among Hamiltonian matrix elements, including those of longer range. The success of the approximation depends basically on whether those contributions to a perturbative expansion for the true self-energy which are contained in the self-consistent approximation are in fact those of major importance: a question which can best be answered by direct consideration of specific applications. A general benefit, however, will be the grouping of various statistical parameters in the renormalization relations. From these groupings the relative importance and interaction of different forms of correlation can be recognized, providing valuable clues to the understanding of the complex variations in real disordered solids.

APPENDIX: SPECTRAL FUNCTIONS FOR THE DIAMOND LATTICE

Collected here are the main formulas used to evaluate Green's functions for the diamond lattice, with a few comments on computational implementation.

The normalized eigenvalues x_i (see Sec. II) for the diamond lattice are given by the dispersion relation[7]

$$4x^2 = 1+\cos\theta_1\cos\theta_2+\cos\theta_2\cos\theta_3 +\cos\theta_3\cos\theta_1 \equiv 1+\alpha_{123}\,, \tag{A1}$$

where the wave vector components θ_j $(j=1,2,3)$ are uniformly distributed between $\pm\pi$. The spectral function $D(\omega)$ defined in Sec. IV can then be written as

$$D(\omega)=\int \frac{f(x)dx}{1-x/\omega}$$
$$=\frac{4\omega^2}{\pi^3}\int\int\int_0^\pi d\theta_1 d\theta_2 d\theta_3[4\omega^2-1-\alpha_{123}) , \tag{A2}$$

which is thus put in a standard form similar to those defined by Morita and Horiguchi[8] and by Joyce,[9] and therefore expressible as a product of complete elliptic integrals of the first kind[10]:

$$D(\omega)=(4/\omega^2)K(k_+)K(k_-) , \tag{A3}$$

with

$$k_\pm^2=\frac{1}{2}\left[1-\left(1-\frac{1}{2\omega^2}\right)\left(1-\frac{1}{\omega^2}\right)^{1/2} \pm\frac{1}{\omega^2}\left(1-\frac{1}{4\omega^2}\right)^{1/2}\right] . \tag{A4}$$

Using the symmetries of $D(\omega)$ we need consider only complex values of ω^2 in the first quadrant. A study of the values of $k_\pm^2$ as ω^2 moves from infinity toward the origin reveals that k_+^2 crosses the real k^2 axis only to right of $k^2=1$, while k_-^2 crosses to the left. For the evaluation of $K(k_-)$, then, we may use the standard arithmetic-geometric mean (AGM) algorithm.[10] Starting with $a_0=1$, $b_0=(1-k^2)^{1/2}$ we iterate

$$a_{n+1}=\tfrac{1}{2}(a_n+b_n) ,$$
$$b_{n+1}=(a_n b_n)^{1/2} , \tag{A5}$$

until $a_N=b_N$ to the desired accuracy. Then

$$\frac{2}{\pi}K(k)=\frac{1}{a_N} . \tag{A6}$$

When principal values of square roots are taken throughout, this produces K for k^2 in the complex plane cut along the real axis to the right of $k^2=1$. For $K(k_+)$ there is also a simple alternative to the analytic continuation formulas of Morita and Horiguchi: In the AGM, all complex square roots are taken with positive imaginary part, which corresponds to cutting the k^2 plane from $k^2=1$ to the *left* along the real axis. This provides a simple and effective algorithm for the computation of $D(\omega)$, from which the Green's function G_0 and G_1 are obtained. The iterative solution of Eqs. (14) then proceeds efficiently.

One way to accelerate the convergence of these iterations is to use a version of the "secant algorithm."[11] Each time a new approximation to Z and F is obtained, one can use it together with values from the preceding evaluation to extrapolate linearly to values for the next evaluation of G_0 and G_1. The extrapolation formulas for Z, would be

$$Z_{n+1}=\frac{Z_n-(Z_n-Z_{n-1})(Z_n-Z1_n)}{(Z_n-Z_{n-1}-Z1_n+Z1_{n-1})} , \tag{A7}$$

where

$$Z1_n=E-c_1G_0(Z_n,F_n)-c_2G_1(Z_n,F_n) . \tag{A8}$$

Similar equations are used for F. This provides quite satisfactory acceleration of the iteraction process, which is useful in the vicinity of the singular points of $D(\omega)$.

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