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Electronic structure of one-dimensional alloys

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The notion of a particular kind of ordering (Markovian) in one-dimensional alloys is introduced. It is shown how, within the context of the tight-binding model, one may obtain a hierarchy of ever better approximations for the electronic density of states of a Markhoff alloy. Some detailed calculations for the case of 1:1 binary alloys with varying degrees of diagonal and off-diagonal disorder are presented. It is found that the second approximation of the hierarchy already gives very fair agreement with known exact results for the density of states. Generalizations of the method to calculate near-neighbor Green's functions and to apply to alloys with more elaborate (generalized Markovian) orderings are discussed.

I. INTRODUCTION

The theory of the electronic structure of alloys is of interest both for its direct application to alloy systems and because of its bearing upon the solution of certain many-body problems.[1-5] Much work has naturally been directed towards three-dimensional alloys, but the recent interest in quasi-one-dimensional materials, such as the charge-transfer salts of tetracyanoquinodimethane (TCNQ), has focused attention on one-dimensional alloys, particularly in connection with the many-body application.[4] Because of the very different connectivity, one may expect the electronic structures of one- and three-dimensional alloys to be markedly different; on the other hand, the low connectivity in one dimension permits considerable theoretical progress to be made in this case. Indeed, exact methods are known[6,7] for obtaining the electronic density of states in one-dimensional alloys; these methods are, however, very tedious in practice, requiring the solution of functional equations. It would be useful to have an efficient and accurate approximation scheme for obtaining the electronic structures of one-dimensional alloys. It is the purpose of this paper to present such a scheme, albeit restricted to a particular kind of ordering of the alloy.

Actually, what will be described is not a single approximation, but a hierarchy of approximations of increasing accuracy (tending in the limit to the exact result). These approximations are formulated within the context of a tight-binding model; indeed, in the theory presented here only nearest-neighbor transfer integrals are allowed. The method can be generalized to take into account more distant transfer integrals, but the formulas are more complicated and the utility of the method decreases rapidly as more distant transfer integrals are included; the scheme is not very suitable for free-electron-like bands.

The approximation scheme permits partial (or complete) ordering of the alloy to be taken into account provided the ordering is of a particular kind which will be called Markovian (by analogy with a Markhoff process). The requirement that the ordering be of this kind does not seem to be very restrictive since it encompasses the whole range of order from separation of phases through random alloys to completely ordered alloys (see Sec. II). In the limit of perfect order all the approximations of the hierarchy coincide with each other and with the exact result (see Sec. III).

The importance of the partially ordered alloy problem in connection with the solution of the Hubbard model has been pointed out by Economou[4] and White who have investigated an approximation scheme somewhat different from that described here.[8] An approximate method for the treatment of partial order in the three-dimensional case has been described by Brouers *et al.*[9]; this approach is closely related to that used here; in fact, the simpler approximations of our hierarchy are very close to a one-dimensional version of this method.

In Sec. II of this paper the nature and properties of what we call Markovian and generalized Markovian ordering are described and illustrated. Section III gives the derivation of the hierarchy of approximations for the density of states, making use of a formula of the continued-fraction kind.[10,14] In the Appendix a new derivation (related to Butler's method[13]) of this formula is given which may be easily adapted to obtain certain other results required in Sec. V.

In Sec. IV, by way of illustration, some detailed calculations of densities of states are presented, some new, and some corresponding to examples previously considered in the literature for which exact results are known.[8] These calculations are all for 1:1 binary alloys with varying degrees of order (from nearly separated phases through random alloys to alloys with nearly $ABABAB\cdots$ ordering) and disorder of either a diagonal or off-diagonal kind. Where comparison with exact results can be made, it is found that the second approximation already gives very fair agreement.

In Sec. V it is shown how the method may be adapted to obtain a hierarchy of approximations for near-neighbor Green's functions. Finally, in Sec. VI some conclusions and some comments on the method and the results obtained are given.

II. MARKOVIAN ORDERING

Consider a one-dimensional substitutional alloy chain with M sites. Suppose the alloy contains s different species of atom which will be numbered $1,2,\ldots,s$. Then a particular configuration of the alloy may be specified by M numbers $\{\alpha_1,\alpha_2,\ldots,\alpha_M\}$ (where $1\leq\alpha_i\leq s$) indicating that site 1 is occupied by an atom of species α_1, site 2 by an atom of species α_2, etc. The nature of the ordering in the alloy is then specified by some distribution function $f(\alpha_1,\alpha_2,\ldots,\alpha_M)$ giving the probability of the occurrence of the particular configuration $\{\alpha_1,\alpha_2,\ldots,\alpha_M\}$.

In the case of purely random alloys, the distribution f is entirely determined when the proportions $N_1,N_2,\ldots,N_s$ of the different constituents are given. These N_α must satisfy the relation $\sum_{\alpha=1}^{s}N_\alpha=1$, and the distribution function is given by

$$f(\alpha_1,\alpha_2,\ldots,\alpha_M)=N_{\alpha_1}N_{\alpha_2}\cdots N_{\alpha_M}\,. \tag{1}$$

For what we will call Markovian ordering the distribution is entirely determined when a set of "transition probabilities" $p_{\alpha\beta}$ $(1\leq\alpha,\beta\leq s)$ are given; $p_{\alpha\beta}$ determines the probability that site $n+1$ is of species β given that site n is of species α (whatever the nature of the species at sites $n-1$, $n-2,\ldots$). The $p_{\alpha\beta}$ must satisfy the constraint

$$\sum_{\beta=1}^{s}p_{\alpha\beta}=1 \quad\text{for all }\alpha, \tag{2}$$

which implies that the matrix of the $p_{\alpha\beta}$ has an eigenvalue 1 with corresponding right eigenvector $(1,1,\ldots,1)$. The corresponding left eigenvector is just $(N_1,N_2,\ldots,N_s)$:

$$\sum_{\alpha=1}^{s}N_\alpha p_{\alpha\beta}=N_\beta\,. \tag{3}$$

The distribution function is easily written down for this kind of ordering; it is

$$f(\alpha_1,\alpha_2,\ldots,\alpha_M)=N_{\alpha_1}p_{\alpha_1\alpha_2}p_{\alpha_2\alpha_3}p_{\alpha_3\alpha_4}\cdots p_{\alpha_{M-1}\alpha_M}\,. \tag{4}$$

Let us give some examples of Markovian ordering.

(i) A purely random alloy corresponds to the choice $p_{\alpha\beta}=N_\beta$ as may be seen by comparing (1) and (4).

(ii) An "alloy" with separated phases corresponds to the choice $p_{\alpha\beta}=\delta_{\alpha\beta}$; $f(\alpha_1,\alpha_2,\ldots,\alpha_M)$ then vanishes unless $\alpha_1=\alpha_2=\alpha_3=\cdots=\alpha_M$, and when this condition is satisfied it takes the value N_{α_1}.

(iii) A binary 1:1 alloy with $ABABAB\cdots$ ordering corresponds to the choice $s=2$ with $p_{11}=p_{22}=0$, $p_{12}=p_{21}=1$; similarly one could represent 1:1:1 ternary alloys with the ordering $ABCABC\cdots$ The way in which other kinds of ordering (e.g., $AABAAB\cdots$) may be brought within the scheme is discussed in Sec. II.

(iv) If the distribution function is determined by some potential W according to

$$f(\alpha_1,\alpha_2,\ldots,\alpha_M)=\exp[-W(\alpha_1,\alpha_2,\ldots,\alpha_M)], \tag{5}$$

then the ordering will be Markovian if to an adequate approximation W can be represented in the form

$$W=\sum_i W_1(\alpha_i)+\sum_i W_2(\alpha_i,\alpha_{i+1})\,, \tag{6}$$

i.e., only nearest-neighbor interactions contribute significantly to W.

As will be seen, the restriction to Markovian ordering is not too severe since it encompasses a wide range of the cases of interest. Further, a specification of the $p_{\alpha\beta}$ will often represent the limit of the information available concerning the nature of the ordering.

In the remainder of this paper we shall be principally concerned with the averages of functions of the $\{\alpha_i\}$ over the $\{\alpha_i\}$ with the weight function $f(\alpha_i)$; both with complete averages of the form

$$\langle h(\alpha_1,\alpha_2,\ldots,\alpha_M)\rangle=\sum_{\alpha_1\alpha_2\cdots\alpha_M}h(\alpha_1,\ldots,\alpha_M)f(\alpha_1,\ldots,\alpha_M) \tag{7}$$

and with conditional averages for which we use the notation

$$\langle h(\alpha_1, \ldots, \alpha_M)\rangle^{\beta_1\beta_2\cdots\beta_k}_{i_1 i_2\cdots i_k} = \frac{\left(\sum_{\alpha_1\cdots\alpha_M} h(\alpha_1, \ldots, \alpha_M) f(\alpha_1, \ldots, \alpha_M)\delta_{\alpha_{i_1}\beta_1}\delta_{\alpha_{i_2}\beta_2}\delta_{\alpha_{i_k}\beta_k}\right)}{\left(\sum_{\alpha_1\cdots\alpha_M} f(\alpha_1, \ldots, \alpha_M)\delta_{\alpha_{i_1}\beta_1}\delta_{\alpha_{i_2}\beta_2}\cdots\delta_{\alpha_{i_k}\beta_k}\right)} \tag{8}$$

so $\langle h\rangle^{\alpha}_{n}$ is the average of h over all configurations in which site n is of type α, $\langle h\rangle^{\alpha\beta}_{nm}$ is the average over all configurations in which site n is of type α and site m is of type β, etc.

Certain relations between conditional averages over Markovian distributions will be needed. These relations, which may be easily derived from (7), (8), and (4) using (2) and (3) are the following: (a) if h is some function of the α_i, then

$$\langle h\rangle = \sum_{\alpha} N_\alpha \langle h\rangle^{\alpha}_{n} \quad \text{for any } n\,; \tag{9}$$

$$\langle h\rangle^{\alpha}_{n} = \sum_{\beta} p_{\alpha\beta}\langle h\rangle^{\alpha\beta}_{n,n+1} = \sum_{\beta} p_{\beta\alpha}\langle h\rangle^{\alpha\beta}_{n,n-1}\,; \tag{10}$$

$$\langle h\rangle^{\alpha\beta}_{n,n+1} = \sum_{\gamma} p_{\beta\gamma}\langle h\rangle^{\alpha\beta\gamma}_{n,n+1,n+2} = \sum_{\gamma} p_{\gamma\alpha}\langle h\rangle^{\gamma\alpha\beta}_{n-1,n,n+1}\,. \tag{11}$$

(b) if $k_n(\alpha_n, \alpha_{n+1}, \ldots, \alpha_M)$ is a function of the α_i with $i \geqslant n$ only, then

$$\langle k_n\rangle^{\alpha}_{n} = \langle k_n\rangle^{\alpha\beta}_{n,n-1} = \langle k_n\rangle^{\alpha\beta\gamma}_{n,n-1,n-2}, \text{ etc.} \tag{12}$$

i.e., for such a function once the condition that site n is of type α is specified, the specification of further conditions at sites $i < n$ is of no consequence; this is the most essential feature of Markovian ordering. Likewise, if $l_n(\alpha_1, \alpha_2, \ldots, \alpha_n)$ is a function of the α_i with $i < n$ only, then

$$\langle l_n\rangle^{\alpha}_{n} = \langle l_n\rangle^{\alpha\beta}_{n,n+1} = \langle l_n\rangle^{\alpha\beta\gamma}_{n,n+1,n+2} = \cdots\,. \tag{13}$$

The notion of Markhoff ordering described above may be quite simply generalized. One may most simply generalize it by introducing a set of "compound transition probabilities" $p_{\alpha\beta\gamma}$ which give the probability that site $n+1$ is of type γ given that sites $n-1, n$ are of types α, β (irrespective of the species at site $n-2$, $n-3, \ldots$). Such a situation would arise, for example, if the distribution function has the form (5), but it is thought necessary to include in W not only the contribution of nearest-neighbor interactions, but also next-nearest-neighbor interactions. The above results may all be generalized in an appropriate way for this "generalized Markovian ordering." The distribution function is

$$f(\alpha_1, \ldots, \alpha_M) = N_{\alpha_1} p_{\alpha_1\alpha_2} p_{\alpha_1\alpha_2\alpha_3} p_{\alpha_2\alpha_3\alpha_4} \cdots p_{\alpha_{M-2}\alpha_{M-1}\alpha_M}\,, \tag{14}$$

where $p_{\alpha\beta} = \sum_\gamma N_\gamma p_{\gamma\alpha\beta}$; (9) and (10) still hold good, but (11) is replaced by

$$\langle h\rangle^{\alpha\beta}_{n,n+1} = \sum_{\gamma} p_{\alpha\beta\gamma}\langle h\rangle^{\alpha\beta\gamma}_{n,n+1,n+2} = \sum_{\gamma} p_{\gamma\alpha\beta}\langle h\rangle^{\gamma\alpha\beta}_{n-1,n,n+1} \tag{15}$$

and (12) is replaced by

$$\langle k_n\rangle^{\alpha\beta}_{n-1,n} = \langle k_n\rangle^{\gamma\alpha\beta}_{n-2,n-1,n} = \langle k_n\rangle^{\eta\gamma\alpha\beta}_{n-3,n-2,n-1,n} = \cdots \tag{16}$$

and so on. Obviously one could further generalize, introducing transition probabilities $p_{\gamma\beta\alpha\eta}$ in which the probability of a species at site $n+1$ depends upon the species at sites n, $n-1$, and $n-2$ and obtain further generalizations of the above formulas. These generalizations depending upon compound transition probabilities $p_{\alpha\beta\gamma}$, $p_{\alpha\beta\gamma\eta}$, $p_{\alpha\beta\gamma\eta\theta}, \ldots$ will be referred to as generalized Markovian orderings of the first, second, third, etc. kinds.

III. ELECTRONIC DENSITY OF STATES

Consider an open chain of $N+N'+1$ sites which will be labeled $-N'$, $-(N'-1), \ldots, -1, 0, 1, 2, \ldots, N-1, N$; the limit $N, N' \to \infty$ is always contemplated. The Hamiltonian for an electron of a substitutional alloy on this chain can be written in the tight-binding approximation (with nearest-neighbor overlap integrals only) for a particular configuration of the alloy as

$$H = \sum_n e_n |n)(n| + \sum_n \left[t_{n+1,n}|n+1)(n| + t_{n,n+1}|n)(n+1|\right], \tag{17}$$

where the sums over n run from $-N'$ to N, $|n)$ is the tight-binding orbital at site n, e_n is the diagonal energy at site n (for the particular configuration), and $t_{n+1,n}$ and $t_{n,n+1}$ are the transfer integrals between sites n and $n+1$; in fact $t_{n+1,n}$

$=t_{n,n+1}$, but it is convenient to distinguish these quantities for the moment. If the alloy is a substitutional one with s species and the configuration to which the Hamiltonian (17) corresponds is that represented by $\{\alpha_{-N}, \alpha_{1-N'}, \ldots, \alpha_0, \ldots, \alpha_N\}$ in the notation of Sec. II, then $e_n = \epsilon_{\alpha_n}$, where $\epsilon_1, \epsilon_2, \ldots, \epsilon_s$) are the diagonal energies corresponding to the species, and $t_{n+1,n} = t_{n,n+1} = t_{\alpha_n \alpha_{n+1}}$ where $t_{\alpha\beta}$ is the transfer integral between species α and β. Pure diagonal disorder corresponds to having all $t_{\alpha\beta}$ equal but distinct ϵ_α, pure off-diagonal disorder to having all ϵ_α equal but distinct $t_{\alpha\beta}$.

The electron Green's function $g_{mn}(z)$ for the particular configuration to which (17) corresponds are defined as the matrix elements of the resolvent $(z-H)^{-1}$:

$$g_{mn}(z) = (m|\,(z-H)^{-1}|n), \tag{18}$$

where H is given by (17) and z is a complex frequency. One is, of course, ultimately interested not in the Green's function for a particular configuration, but rather in the averaged Green's functions

$$G_{mn}(z) = \langle g_{mn}(z)\rangle , \tag{19}$$

where the average is over all configurations with the appropriate weight i.e., just an average of the kind defined in Sec. II. In particular, the average electronic density of states per site $\rho(\epsilon)$ for the alloy can be expressed in terms of $G_{00}(z)$:

$$\rho(\epsilon) = \frac{1}{\pi} \lim_{\eta \to 0+} \operatorname{Im} G_{00}(\epsilon - i\eta) , \tag{20}$$

where Im means the imaginary part and the limit $N, N' \to \infty$ has been taken.

A formula for the Green's function g_{00} (in the limit $N, N' \to \infty$) has been derived by Economou and Cohen,[10] namely,

$$g_{00}(z) = [z - e_0 - t_{01}^2 \delta_1(z) - t_{0,-1}^2 \delta_{-1}(z)]^{-1} , \tag{21}$$

where $\delta_{\pm n}(z)$ (for $n = 1, 2, 3, \ldots$) are the infinite continued fractions

$$\delta_{\pm n}(z) = \cfrac{1}{z - e_{\pm n} - \cfrac{t^2_{\pm(n+1), \pm n}}{z - e_{\pm(n+1)} - \cfrac{t^2_{\pm(n+2), \pm(n+1)}}{z - e_{\pm(n+2)} - }}} \tag{22}$$

satisfying the recurrence relation

$$\delta_{\pm n}(z) = [z - e_{\pm n} - t^2_{\pm n, \pm(n+1)} \delta_{\pm(n+1)}(z)]^{-1} . \tag{23}$$

Cohen and Economou derived (21) by a graphical analysis; it may also be obtained by the continued-fraction method[14]; for the reasons explained in the Introduction we have given an alternative derivation in the Appendix.

The simplest of the hierarchy of approximations may be based directly upon (21) and (23). We introduce the average (using the notation of Sec. II)

$$\Delta_\alpha(z) = \langle \delta_n(z)\rangle_n^\alpha , \quad n \geq 1 \tag{24}$$

which is independent of n (in the limit $N, N' \to \infty$). We assume the ordering to be of a Markovian kind and combine (23), (24), and (10) to obtain

$$\Delta_\alpha(z) = \langle [z - e_n - t^2_{n,n+1} \delta_{n+1}(z)]^{-1} \rangle_n^\alpha$$

$$= \sum_\beta p_{\alpha\beta} \langle (z - e_n - t^2_{n,n+1}\delta_{n+1})^{-1}\rangle^{\alpha\beta}_{n,n+1} . \tag{25}$$

The simplest approximation is now obtained by approximating the right-hand side of (25) according to

$$\Delta_\alpha(z) = \sum_\beta p_{\alpha\beta} (z - \epsilon_\alpha - t^2_{\alpha\beta} \langle \delta_{n+1}\rangle^{\alpha\beta}_{n,n+1})^{-1} \tag{26}$$

and using (11) to write

$$\langle \delta_{n+1}(z)\rangle^{\alpha\beta}_{n,n+1} = \langle \delta_{n+1}(z)\rangle^\beta_{n+1} = \Delta_\beta(z) \tag{27}$$

since $\delta_{n+1}(z)$ is a function of $\alpha_{n+1}, \alpha_{n+2}, \ldots$, but not of the α_i with $i \leq n$. Then the approximation (26) gives the equation

$$\Delta_\alpha(z) = \sum_\beta \frac{p_{\alpha\beta}}{z - \epsilon_\alpha - t^2_{\alpha\beta}\Delta_\beta(z)} \tag{28}$$

for $\Delta_\alpha(z)$.

By a similar argument one may also show that (for $n \geq 1$)

$$\langle \delta_{-n}(z)\rangle^\alpha_{-n} = \Delta_\alpha(z) . \tag{29}$$

To obtain $G_{00}(z)$ one starts from (21) and uses (9) and (10) to write

$$G_{00}(z) = \sum_{\alpha\beta\gamma} p_{\beta\alpha} N_\alpha p_{\alpha\gamma} \langle [z - e_0 - t^2_{0,-1}\delta_{-1}(z) - t^2_{01}\delta_1(z)]^{-1}\rangle^{\beta\alpha\gamma}_{-1,0,1}$$

$$\simeq \sum_{\alpha\beta\gamma} p_{\beta\alpha} N_\alpha p_{\alpha\gamma} [z - \epsilon_\alpha - \langle t^2_{\alpha\beta}\delta_{-1}(z) + t^2_{\alpha\gamma}\delta_1(z)\rangle^{\beta\alpha\gamma}_{-1,0,1}]^{-1} , \tag{30}$$

where an approximation corresponding to (26) has been made at the last step. Since $\delta_1(z)$ depends only upon the α_i with $i \geq 1$, and $\delta_{-1}(z)$ only upon the α_i with $i \leq -1$, one may now use (11), (12), (13), (24), and (29) to write

$$\langle t^2_{\alpha\beta}\delta_{-1}(z)+t^2_{\alpha\beta}\delta_1(z)\rangle^{\beta\,\alpha\gamma}_{-1,0,1}=t^2_{\alpha\beta}\Delta_\beta(z)+t^2_{\alpha\gamma}\Delta_\gamma(z) \tag{31}$$

and (30) becomes

$$G_{00}(z)=\sum_{\alpha\beta\gamma}\frac{p_{\beta\alpha}N_\alpha p_{\alpha\gamma}}{z-\epsilon_\alpha-t^2_{\alpha\beta}\Delta_\beta(z)-t^2_{\alpha\gamma}\Delta_\gamma(z)}\,. \tag{32}$$

Equations (28), (32), and (20) now form a complete set to determine $\Delta_\alpha(z)$, $G_{00}(z)$, and $\rho(\epsilon)$, and together constitute the simplest approximation of the hierarchy.

To obtain the next approximation for $\Delta_\alpha(z)$ one iterates (23) once, substitutes the result into (24), and makes an approximation similar to (26), obtaining

$$\begin{aligned}\Delta_\alpha(z)&=\left\langle\left(z-e_n-\frac{t^2_{n,n+1}}{z-e_{n+1}-t^2_{n+2,n+1}\delta_{n+2}}\right)^{-1}\right\rangle^{\alpha}_{n}\\&=\sum_{\beta\gamma}p_{\alpha\beta}p_{\beta\gamma}\left\langle\left(z-\epsilon_\alpha-\frac{t^2_{\alpha\beta}}{z-\epsilon_\beta-t^2_{\beta\gamma}\delta_{n+2}}\right)^{-1}\right\rangle^{\alpha\beta\gamma}_{n,n+1,n+2}\\&\simeq\sum_{\beta\gamma}p_{\alpha\beta}p_{\beta\gamma}\left(z-\epsilon_\alpha-\frac{t^2_{\alpha\beta}}{z-\epsilon_\beta-t^2_{\beta\gamma}\langle\delta_{n+2}\rangle^{\alpha\beta\gamma}_{n,n+1,n+2}}\right)^{-1}\end{aligned}$$

i.e., using (12),

$$\Delta_\alpha(z)=\sum_{\beta\gamma}\frac{p_{\alpha\beta}p_{\beta\gamma}}{z-\epsilon_\alpha-\dfrac{t^2_{\alpha\beta}}{z-\epsilon_\beta-t^2_{\beta\gamma}\Delta_\alpha(z)}} \tag{33}$$

which replaces (25) in the second approximation. By a similar analysis, the corresponding approximation for $G(z)$ is

$$G_{00}(z)=\sum_{\alpha\beta\gamma\eta\theta}\frac{p_{\alpha\beta}p_{\beta\alpha}N_\alpha p_{\alpha\eta}p_{\eta\theta}}{z-\epsilon_\alpha-\dfrac{t^2_{\alpha\beta}}{z-\epsilon_\beta-t^2_{\beta\gamma}\Delta_\gamma}-\dfrac{t^2_{\alpha\eta}}{z-\epsilon_\eta-t^2_{\eta\theta}\Delta_\theta}}\,. \tag{34}$$

Obviously one can proceed in this way to obtain a whole hierarchy of approximations for $\Delta_\alpha(z)$ by iterating (23) some number of times, substituting the result in (24) and then carrying out an approximation of the kind used in deriving (26) and (33). In each case one may obtain a corresponding approximation for $G_{00}(z)$ and the density of states. As one continues this process to higher and higher orders, one approaches more and more closely to a direct evaluation of the average of the expression (21) for $g_{00}(z)$ with $\delta_{\pm1}(z)$ substituted from (22), so in the limit this hierarchy of approximations tends to the exact result. In fact, where comparisons have been made (see Sec. IV) it is found that the second approximation derived above is already in quite fair agreement with the exact results.

The formulas derived above may be modified to apply to cases with generalized Markovian ordering. For example, in the case of generalized Markovian ordering of the first kind (see Sec. II), one would introduce instead of $\Delta_\alpha(z)$ the quantity

$$\begin{aligned}\Delta_{\alpha\beta}(z)&=\langle\delta_n\rangle^{\alpha\beta}_{n-1,n}\\&=\langle(z-e_n-t^2_{n,n+1}\delta_{n+1})^{-1}\rangle^{\alpha\beta}_{n-1,n}\end{aligned} \tag{35}$$

using (23). Now, making use of the approximation (26) and the formulas (15) and (16) one may obtain the equation

$$\Delta_{\alpha\beta}(z)=\sum_{\gamma}\frac{p_{\alpha\beta\gamma}}{z-\epsilon_\beta-t^2_{\beta\gamma}\Delta_{\beta\gamma}} \tag{36}$$

for $\Delta_{\alpha\beta}$, the generalization of (25). Likewise (32) is generalized to

$$G_{00}(z)=\sum_{\alpha\beta\gamma}\frac{N_\alpha p_{\alpha\beta\gamma}}{z-\epsilon_\beta-t^2_{\alpha\beta}\Delta_{\alpha\beta}(z)-t^2_{\beta\gamma}\Delta_{\beta\gamma}(z)}\,. \tag{37}$$

In a similar way any of the approximations of the hierarchy may be generalized to the case of generalized Markovian ordering of the first kind, or, indeed, generalized Markovian ordering of any kind.

In some cases when the Markovian ordering tends to perfect order the simplest approximation becomes exact (as do all the higher-order approximations). Consider, for example, a 1:1 binary alloy; possible ordered states are states with separated phases and states with *ABABAB* $\cdots$ ordering. In each case when it is given that site n is of type A or B the species at all other sites are completely determined by the $p_{\alpha\beta}$, since $p_{11}=p_{22}=1$ and $p_{12}=p_{21}=0$ in the one case and $p_{11}=p_{22}=0$ and $p_{12}=p_{21}=1$ in the other case. Thus in these cases only a single configuration contributes to an average of the form $\langle h\rangle_n^{\alpha}$ and approximations such as (26) actually become exact, making the simplest approximation exact.

The same remarks apply to any "alloy" which is ordered in the sense that it has separated phases. Also to three-, four, ..., component alloys with orderings of the type *ABCABCABC*..., *ABCDABCD*..., etc. However, the same is not true, for example, in the case of a 2:1 binary alloy with the ordering *AABAABAAB* $\cdots$. In this case $p_{11}=p_{12}=\frac{1}{2}$, $p_{22}=0$, $p_{21}=1$, and given that site n is of type A the $p_{\alpha\beta}$ no longer determine uniquely the species at other sites. The truth of the matter is that ordering of this kind cannot be specified as a limit of a simple Markovian ordering. It may, however, be specified as a limiting case of a generalized Markovian ordering of the first kind (with $p_{112}=p_{121}=p_{211}=1$ and other $p_{\alpha\beta\gamma}=0$), and so can be treated using the generalization to this case discussed above, which one can now show to become exact in the ordered limit.

By similar arguments one may show that any perfect ordering is a limit of a generalized Markovian ordering of some kind and that the corresponding generalized approximations become exact in the ordered limit.

IV. DENSITY OF STATES FOR BINARY ALLOYS

In order to illustrate the approximations derived in Sec. III and to assess the accuracy of the method by comparison with known exact results, a number of detailed calculations of the density of states have been carried out for 1:1 binary alloys. For such alloys the $p_{\alpha\beta}$ satisfying the constraints (2) and (3) may all be expressed in terms of a single parameter p on the range (0, 1) according to

$$p_{11}=p_{22}=p,\quad p_{12}=p_{21}=1-p\ . \tag{38}$$

The limit $p=1$ corresponds to the formation of separated phases, $p=0$ to an alloy with *ABABAB* $\cdots$ ordering and $p=\frac{1}{2}$ to a random alloy.

The first of the calculations to be described are concerned with cases of purely diagonal disorder, i.e., we take $t_{11}=t_{12}=t_{21}=t_{22}=-t$ (with $t>0$), but allow ϵ_1 and ϵ_2 to differ. In fact, with a suitable choice for the origin of energy one may take

$$\epsilon_1=-\epsilon_2=\tfrac{1}{2}\delta t \tag{39}$$

so the degree of disorder is defined (relative to the transfer integral t) by the parameter δ. In the limit $\delta=0$ of no disorder, one would obtain an ordinary one-dimensional tight-binding band of width $4t$ with the dispersion relation $\epsilon(k)=-2t\cos k$ and density of states per site

$$t\rho(\epsilon)=\begin{cases}(1/\pi)[4-(\epsilon/t)^2]^{-1/2} & \text{if } |\epsilon/t|<2\\ 0 & \text{if } |\epsilon/t|>2\end{cases} \tag{40}$$

which diverges at the ends of the band because of the Van Hove singularities at $k=\pm\pi$.

In the limit of separated phases ($p=1$) and finite δ, $\rho(\epsilon)$ is a superposition of the densities of states for the separate A and B bands, each of which is of the form (40) but displaced by $\pm\frac{1}{2}\delta t$:

$$t\rho(\epsilon)=\frac{1}{2\pi}\left[4-\left(\frac{\epsilon}{t}+\frac{\delta}{2}\right)^2\right]^{-1/2}+\frac{1}{2\pi}\left[4-\left(\frac{\epsilon}{t}-\frac{\delta}{2}\right)^2\right]^{-1/2} \tag{41}$$

(with the understanding that each term is to be replaced by 0 if the argument of the square root becomes negative); the two bands overlap if $\delta<4$. In the opposite limit ($p=0$) of *ABABAB* $\cdots$ ordering, the density of states is that appropriate to the corresponding band structure:

$$t\rho(\epsilon)=\begin{cases}\dfrac{1}{\pi}\left(\dfrac{\epsilon}{t}\right)\left[\left(\dfrac{\epsilon}{t}\right)^2-\left(\dfrac{\delta}{2}\right)^2\right]^{-1/2}\left[4+\left(\dfrac{\delta}{2}\right)^2-\left(\dfrac{\epsilon}{t}\right)^2\right]^{-1/2}\\ \text{if } \delta/2<|\epsilon/t|<[4+(\delta/2)^2]^{-1/2}\\ 0\quad\text{otherwise;}\end{cases} \tag{42}$$

it consists of two bands symmetric about the origin, the upper band extending from $\frac{1}{2}\delta t$ to $2t[1+(\delta/4)^2]^{1/2}$; again there are Van Hove singularities at the ends of the bands. It will be seen that in all these cases $\rho(\epsilon)$ is an even function of ϵ [relative to the origin of energy determined by (39)]; in fact, one may show that for this model $\rho(\epsilon)$ is even for all values of p.

In order to solve equations like (28) and (33) numerically, the procedure suggested by White and Economou[8] was adopted. Actually these equations are equivalent to polynomial equations for $\Delta_\alpha(z)$ with coefficients which are polynomials in z. Thus $\Delta_\alpha(z)$ is a many-valued function of z. However, all the branch points lie on the real axis, so it suffices to introduce branch cuts along the real axis in order to ensure that $G_{00}(z)$ has the correct analytical properties. It is still necessary to ensure that one has found the correct branch of

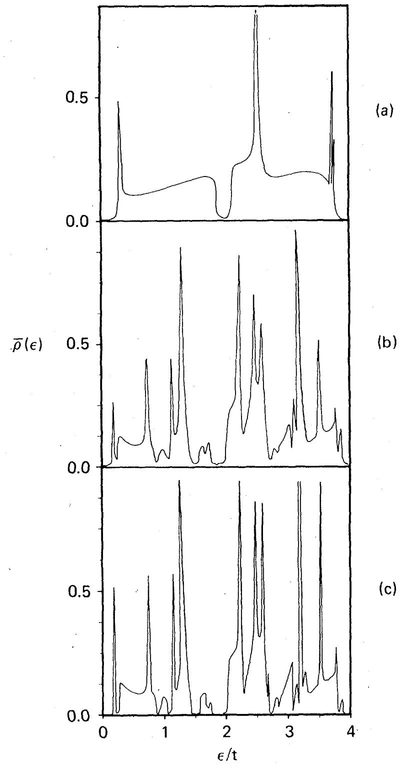

FIG. 1. Various calculations of the density of states $\bar{\rho}(\epsilon)$ for the case $\delta=4$, $p=\frac{1}{2}$ (see text); (a) calculated using the first approximation and coarse grained with $\eta=0.02t$ (see text); (b) calculated in the second approximation with same coarse graining; (c) calculated in the second approximation with little coarse graining ($\eta=0.002t$).

$\Delta_\alpha(z)$. In order that $G_{00}(z)$ have the correct behavior as $z\to\infty$ it is necessary that $\Delta_\alpha(z)\to 0$ as $z\to\infty$. One may show that there is just one branch of $\Delta_\alpha(z)$ with this property and that for this branch $\Delta_\alpha(z)\sim 1/z$ as $z\to\infty$. The equations (28) and (33) were accordingly solved by the following procedure: starting at a large value of ϵ with the asymptotic solution $\Delta_\alpha(z)\simeq 1/z$ the equations were solved at a succession of points on the line $z=\epsilon+0.05i$ (ϵ real) in the complex plane by a Newton-Raphson procedure; then, starting at each of the points $\epsilon_n+0.05i$ thus calculated they were solved at points ϵ_n+xi with x decreasing from 0.05 towards 0 (again by a Newton-Raphson procedure) to obtain $\Delta_\alpha(z)$ at the points $\epsilon_n+i\eta$ with η very small. $G_{00}(\epsilon+i\eta)$ and $\rho(\epsilon)$ were then evaluated using the formulas (30) or (34) and (20).

The $\rho(\epsilon)$ calculated by this procedure can in some cases show very sharp peaks [see, for example, Fig. 1(c)], making graphical presentation difficult and requiring the use of a very fine mesh in ϵ to faithfully represent them. Furthermore, in this form they are not directly comparable with precise results[8] which are only available as histograms giving $\rho(\epsilon)$ averaged over some interval $\Delta\epsilon$. To circumvent these complications we have mainly calculated not the true $\rho(\epsilon)$, but a slightly coarse-grained average $\bar{\rho}(\epsilon)$, obtained by the simple expedient of calculating $\bar{\rho}(\epsilon)=(1/\pi)\operatorname{Im}G_{00}(\epsilon+i\eta)$ at a small finite value of η (usually $\eta=0.02t$). The effect of this coarse graining is illustrated in one (fairly extreme) case by a comparison of Figs. 1(b) and 1(c), calculated in the second approximation for the case $\delta=4$, $p=\frac{1}{2}$ with $\eta=0.02t$ [Fig. 1(b)] and with $\eta=0.002t$ [Fig. 1(c)]. In all the other figures presented here, coarse graining with $\eta=02t$ has been used. This coarse graining introduces one rather irritating artefact which may be noted in a comparison of Figs. 1(b) and 1(c), namely, the nonvanishing of $\bar{\rho}(\epsilon)$ for some values of ϵ at which $\rho(\epsilon)$ actually vanishes; this arises because the averaging is of a Lorentzian kind with long wings.

Calculations were carried out using both the first and the second approximations of the hierarchy described in Sec. III. Comparison with results[8] obtained by the Schmidt method[7] showed the second approximation to be far better than the first. All the results presented here were calculated in the second approximation with the exception of Fig. 1(a). In Fig. 1(a) the first-order approximation for $\bar{\rho}(\epsilon)$ is shown for the case $\delta=4$, $p=\frac{1}{2}$ for the sake of comparison with the corresponding second-approximation result of Fig. 1(b) (actually, of all the cases examined, this is the one in which the first approximation is at its poorest compared to the second).

In Fig. 2, $\bar{\rho}(\epsilon)$ has been plotted for varying degrees of diagonal disorder δ and for varying degrees of order ranging from $p=0.9$ (close to separation of phases) through $p=0.5$ (random alloy) to $p=0.1$ (close to $ABABAB\cdots$ order). The results corresponding to $p=0.9$, 0.5, 0.1 are comparable to the exact results for these cases given by White and Economou[8] which are also shown in Figure 2. Such comparisons show that the second approximation gives quite a fair account of $\rho(\epsilon)$; some peaks of $\rho(\epsilon)$ in the exact result are missed by the approximation and the troughs given by the approximation are not as deep as they should be; the greater height of some peaks in Fig. 2 when compared with White and Economou's exact results is simply a consequence of the fact that we have used averaging over a smaller width ($\Delta\epsilon=0.02t$) than was used in the Schmidt calculation histograms ($\Delta\epsilon=0.05t$).

It would be possible by an examination of additional data available, such as, for example, the partial densities of states $\rho_A(\epsilon)$, $\rho_B(\epsilon)$ at the A

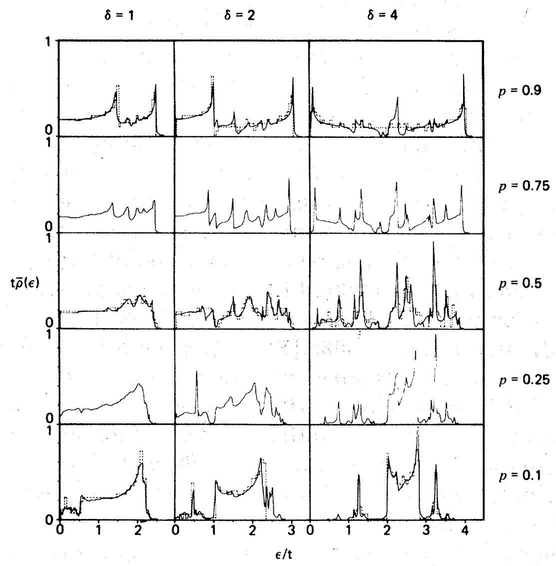

FIG. 2. Coarse-grained ($\eta = 0.02t$) densities of states $\bar{\rho}(\epsilon)$ calculated in the second approximation for several values of the order parameter p and varying degrees of diagonal disorder δ (see text) (solid line). The broken lines give the comparable exact results obtained by the Schmidt method.[8]

and B sites and the near-neighbor Green's functions to be discussed in Sec. V, to ascertain in detail the physical features giving rise to the complicated structures shown in Fig. 2, but this would seem to serve little purpose. We shall therefore make only a few very general comments on these results.

The peaks in $\rho(\epsilon)$ arise from two causes. For small values of δ they are ghosts of the Van Hove singularities of (41) and (42) and occur for p near to 0 or 1. As δ increases $\rho(\epsilon)$ becomes increasingly peaky, especially for middle values of p, because of increasing localization of some alloy wave functions. Clusters of atoms of a particular configuration will occur with various frequencies; wave functions strongly localized on a frequently occurring type of cluster will give rise to a peak in $\rho(\epsilon)$ at the appropriate energy. The width of this peak will reflect the degree to which this energy is affected by the environment of the cluster and how easily it may communicate with similar localized wave functions of nearly matching energy on neighboring clusters. So, as localization becomes stronger, the peaks will become narrower and higher. In the cases $p = 0.1$ and $p = 0.9$ the bands corresponding to (41) and (42) can be seen forming, reflecting in the first case the presence of regions of the forms $AAAA\cdots$ and $BBBB\cdots$ and in the second case regions of the form $ABABAB\cdots$. The additional peaks in the $p = 0.1$ case can be interpreted as due to wave functions localized on isolated clusters and with energies not matching those of the bands. Regarding the question of the formation of gaps in the spectrum, some systematics can be observed. For $\delta > 4$ a gap forms around $\epsilon = 0$ for all values of p as expected. For $p = 0.1$ this tendency is strong for all values of δ, reflecting the fact that there is a gap in the spectrum (42) for all values of δ. There is a systematic tendency for a gap to form close to $\frac{1}{2}\delta t$ for all values of p other than those close to 1. Beyond this, the formation of gaps seems to be associated with the increased peakiness as δ increases, i.e., the tendency to form an isolated line spectrum.

Calculations were also carried out for some cases of purely off-diagonal disorder. Again the 1:1 binary alloy was studied, but in this case we set $\epsilon_1 = \epsilon_2 = 0$ and

$$t_{11} = \xi t, \quad t_{12} = t_{21} = t, \quad t_{22} = t/\xi \tag{43}$$

so the disorder was measured by the single parameter ξ. In the limit $p = 1$ of separated phases the density of states is a superposition of two bands of the form (40) but different widths:

$$t\rho(\epsilon) = \frac{1}{2\pi\xi^2}\left[4\xi^2 - \left(\frac{\epsilon}{t}\right)^2\right]^{-1/2} + \frac{\xi^2}{2\pi}\left[\frac{4}{\xi^2} - \left(\frac{\epsilon}{t}\right)^2\right]^{-1/2} \tag{44}$$

with Van Hove singularities at $\epsilon/t = \pm 2\xi, \pm 2/\xi$. In the limit $p = 0$ the density of states is again given by (40).

The calculations were all carried out in the second approximation by the numerical procedure described above and averaging with $\eta = 0.02t$ was again used; $\rho(\epsilon)$ remains an even function of ϵ. The results for the values $\xi = \sqrt{2}$, $\xi = 2$, and various p are shown in Fig. 3. Again some strong peaks can be seen. In this case one would not expect the development of systematic gaps in the spectrum, and the gaps found are associated with the peaky parts of the spectrum.

V. NEAR-NEIGHBOR GREEN'S FUNCTIONS

The theory of Sec. III may be extended to calculate other averaged Green's functions $G_{mn}(z)$, but the method appears to be convenient only if n and m are close neighbors. Consider first the nearest-neighbor Green's function $G_{10}(z) = \langle g_{10}(z)\rangle$ were $g_{10}(z)$ is given by (18). As discussed in the Appendix, g_{10} may be expressed as

$$g_{10}(z) = -\frac{d}{dt_{01}} \ln |z - H| , \tag{45}$$

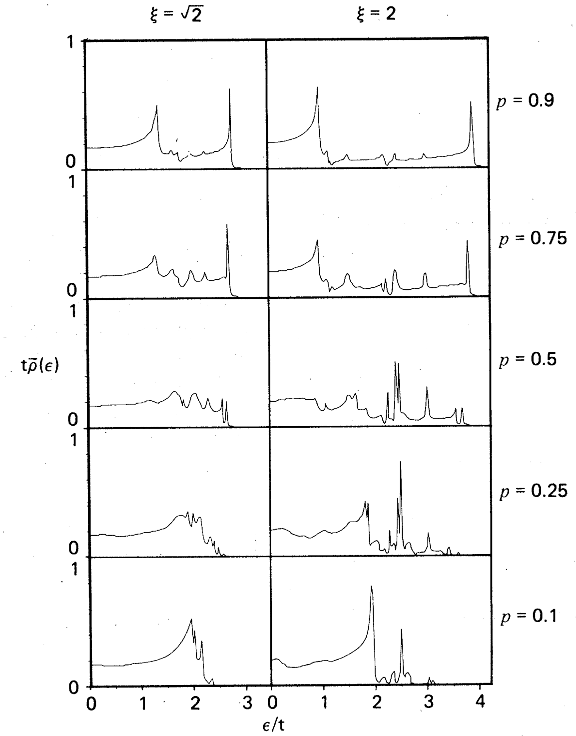

FIG. 3. Coarse-grained ($\eta = 0.02t$) densities of states $\bar{\rho}(\epsilon)$ calculated in the second approximation for several values of the order parameter p and two values of the off-diagonal disorder parameter ξ (see text).

where $|z - H|$ is the determinant of the matrix $(m|\, z - H|n)$ in the notation of Sec. III.

The simplest approximation for G_{10} [equivalent in accuracy to the first approximation for $\rho(\epsilon)$] is obtained by using the expression (A9) for $|z - H|$, namely,

$$\ln|z - H| = \ln(z - e_0 - t_{10}t_{01}\delta_1 - t_{-1,0}t_{0,-1}\delta_{-1}) + X \;, \tag{46}$$

where X represents terms not depending upon t_{01}. Differentiating (46) with respect to t_{01} (note that $\delta_{\pm 1}$ do not depend upon t_{01}), using (45) and averaging

$$\begin{aligned} G_{10}(z) &= \langle t_{01}\delta_1(z - e_0 - t_{10}t_{01}\delta_1 - t_{-1,0}t_{0,-1}\delta_{-1})^{-1}\rangle \\ &= \sum_{\alpha\beta\gamma} N_\alpha p_{\gamma\alpha} p_{\alpha\beta} \langle t_{01}\delta_1 (z - e_0 - t_{10}t_{01}\delta_1 \\ &\qquad\qquad - t_{-1,0}t_{0,-1}\delta_{-1})^{-1}\rangle^{\gamma\alpha\beta}_{-1,0,1} \\ &\simeq \sum_{\alpha\beta\gamma} \frac{N_\alpha p_{\gamma\alpha} p_{\alpha\beta} t_{\alpha\beta}\Delta_\beta}{z - \epsilon_\alpha - t^2_{\alpha\beta}\Delta_\beta - t^2_{\alpha\gamma}\Delta_\gamma} \end{aligned} \tag{47}$$

using an approximation of the kind used in (26); this is the simplest approximation for G_{10}.

To obtain the next approximation in the hierarchy for G_{10} one uses instead of (46) another expression for $|z - H|$, namely (see Appendix),

$$\ln|z - H| = \ln\begin{vmatrix} z - e_{-1} - t^2_{-1,-2}\delta_{-2} & -t_{0,-1} & 0 \\ -t_{-1,0} & z - e_0 & -t_{10} \\ 0 & -t_{01} & z - e_1 - t^2_{12}\delta_2 \end{vmatrix} + X\,, \tag{48}$$

where X again stands for terms not depending upon t_{01}. Differentiating (48), averaging, and approximating in the usual way one obtains

$$G_{10}(z) = \sum_{\alpha\beta\gamma\eta\theta} \frac{p_{\theta\gamma} p_{\gamma\alpha} N_\alpha p_{\alpha\beta} p_{\beta\eta} t_{\alpha\beta}}{[z - \varepsilon_\alpha - t^2_{\gamma\alpha}/(z - \varepsilon_\gamma - t^2_{\gamma\theta}\Delta_\theta)](z - \varepsilon_\beta - t^2_{\beta\eta}\Delta_\eta) - t^2_{\alpha\beta}} \tag{49}$$

Proceeding in this way one can obtain a hierarchy of approximation for G_{10} analogous to those for G_{00}.

In the case of G_{20} the simplest approximation is that corresponding to the second approximation of the hierarchy for G_{00}. It is obtained by averaging and approximating the expression (see Appendix)

$$g_{20}(z) = \frac{d}{dx}\ln\begin{vmatrix} z - e_{-1} - t^2_{-1,-2}\delta_{-2} & -t_{0,-1} & 0 \\ -t_{-1,0} & z - e_0 & -t_{10} \\ x & -t_{01} & z - e_1 - t^2_{12}\delta_2 \end{vmatrix}, \tag{50}$$

where one must put $x = 0$ after differentiation. Again a hierarchy of approximations can be obtained for G_{20}. One finds by similar arguments that the simplest approximation for G_{n0} corresponds to the nth approximation in the hierarchy for G_{00}, and as n increases the calculations become increasingly complex.

Figure 4 shows some examples of the spectral weight function $\bar{\rho}_{10}(\varepsilon)$ (per site) calculated using the approximation (49) [and hence comparable for the corresponding cases with the $\rho(\varepsilon)$ shown in Figs. 2 and 3]; $\bar{\rho}_{10}(\varepsilon)$ has been averaged in the same way as $\rho(\varepsilon)$, taking $\eta = 0.02t$; $\rho_{10}(\varepsilon)$ can be shown to be real and to be an odd function of ε. In general, $\rho_{10}(\varepsilon)$ appears to be of the form $\rho(\varepsilon)r(\varepsilon)$, where $r(\varepsilon)$ is a comparatively slowly varying function of ε, although some exceptions to this rule can be seen.

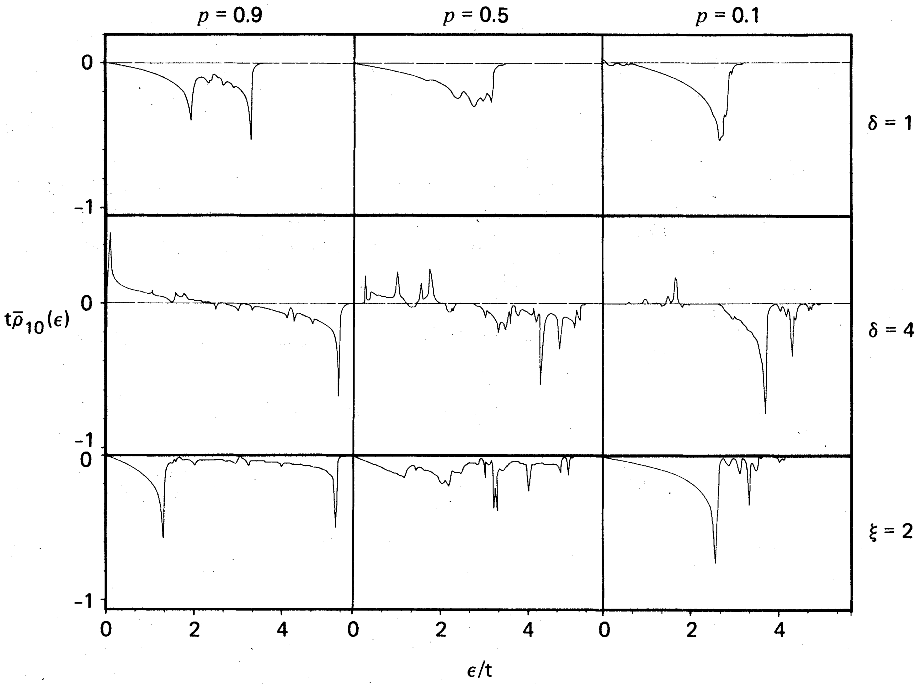

FIG. 4. Coarse-grained ($\eta = 0.02t$) spectral weight functions $\bar{\rho}_{10}(\epsilon)$ of the nearest-neighbor Green's function G_{10} calculated in the second approximation for several values of the order parameter p and varying degrees of diagonal (δ) and off-diagonal (ξ) disorder.

VI. CONCLUSIONS AND COMMENTS

It has been found that, within the context of the tight-binding model and Markovian ordering, the approximation scheme of Sec. III provides a means of obtaining very good approximations to the density of states (becoming exact in the limit of perfect ordering) at a rather low cost in numerical effort. The equations of the approximation scheme [e.g., Eqs. (28), (32), (33), and (34)] are natural and have a simple physical interpretation, as will be explained later in this section. The method may be readily generalized to more elaborate orderings and to calculate near-neighbor Green's functions.

One of the motivations for the construction of this approximation scheme is its possible application in connection with many-body problems, so some comment upon such applications is in order. First, it should be noted that the one-dimensional many-body application often leads to subsidiary alloy problems in which the ordering is of a Markovian or generalized Markovian kind. For example, the method of Cyrot[3] for the Hubbard model leads to distribution functions of the form (5) and (6) which it has been shown represent Markovian orderings in the one-dimensional case. One may also show that to a good approximation the distortions associated with charge-density waves or Peierls' instabilities are of a Markovian nature.

Some of the results obtained in Sec. IV sound a note of warning concerning the approximations often used in passing from a many-body to a related alloy problem (in the one-dimensional case, at least). It was noted in Sec. IV that the density of states may sometimes be very peaky and the peaks very narrow. This is characteristic of the true alloy problem in one dimension and depends upon the fact that the ε_α and $t_{\alpha\beta}$ are fixed and unvarying in time. In the many-body application, however, the quantities equivalent to the ε_α are, in fact, really time-dependent fields; the approximation usually made is to replace them by static fields. However, if these fields should really vary on a time scale τ, peaks in the density of states with widths less than $\hbar/\tau$ are artefacts of the use of the static approximation. In the case of the Hubbard model one is faced with the problem of dealing with what was called the "resonance-broadening" problem.[11]

Finally we remark that, within the limitations of the particular model studied here, the hierarchy of approximations derived in Sec. III represents a complete solution of what is sometimes called the "cluster embedding" problem. This embedding problem is concerned with the question of finding a way to adapt precise calculations on small clusters of atoms to somehow represent the influence on the cluster of the rest of the system, this influence being calculated self-consistently from the solution for the cluster; the Bethe-Peierls method[12] is an example of such a theory. To see how the approximation scheme of Sec. III is connected with this embedding problem, consider what one would get if, for example, one put $\Delta_\gamma = \Delta_\theta = 0$ in (34). One would obtain exactly the on-site Green's function for the middle atom of a cluster of three atoms. The role of the $\Delta_\gamma, \Delta_\theta$ is clearly to approximately represent the influence of the rest of the chain on this cluster (insofar as it affects this particular Green's function). Equation (33) is then, in effect, the self-consistent equation to determine the quantity Δ_α representing this influence. As one passes to higher-order approximations of the hierarchy, one is in effect studying the embedding of larger and larger clusters. The scheme proposed by Brouer *et al.*[9] has the same character, but implementation is much more difficult in three dimensions than in one dimension.

APPENDIX

In this Appendix the derivation of formulas (21), (22), (23), (45), (48), and (50) is outlined. By the ordinary rules for differentiation of determinants and the definition (18) one has

$$g_{00}(z) = -\frac{d}{de_0} \ln|z - H| , \tag{A1}$$

where $|z - H|$ is the determinant of the matrix $(m|z - H|n)$ with H given by (17). It is convenient to introduce the notation

$$D_{N',N}(a_{-N'}, a_{1-N'}, \ldots, a_{-1}, a_0, a_1, \ldots, a_{N-1}, a_N) = \begin{vmatrix} a_{-N'} & t_{-N',1-N'} & & & & & & & \\ t_{1-N',-N'} & a_{1-N'} & \ddots & & & & & 0 & \\ & \ddots & \ddots & \ddots & & & & & \\ & & \ddots & a_{-1} & t_{-1,0} & & & & \\ & & & t_{0,-1} & a_0 & t_{10} & & & \\ & 0 & & & t_{01} & a_1 & \ddots & & \\ & & & & & \ddots & \ddots & a_{N-1} & t_{N-1,N} \\ & & & & & & \ddots & t_{N,N-1} & a_N \end{vmatrix} \tag{A2}$$

for the determinant (A2). Then $|z - H|$ is simply $D_{N',N}(a_{-N'}, \ldots, a_N)$ with a_i replaced by $z - e_i$ for $i = -N', \ldots, N$.

By pivotal condensation on the $(N, N-1)$ element one finds

$$D_{N',N}(a_{-N'}, \ldots, a_N) = D_{N',N-1}(a_{-N'}, \ldots, a_{N-2}, a'_{N-1}) a_N , \tag{A3}$$

where

$$a'_{N-1} = a_{N-1} - t_{N-1,N} t_{N,N-1} / a_N . \tag{A4}$$

Similarly, by pivotal condensation on the $(1-N', -N')$ element

$$D_{N',N}(a_{-N'}, \ldots, a_N) = D_{N'-1,N}(a'_{1-N'}, a_{2-N'}, \ldots, a_N) a_{-N'} , \tag{A5}$$

where

$$a'_{1-N'} = a_{1-N'} - t_{-N',1-N'} t_{1-N',-N'} / a_{-N'} . \tag{A6}$$

Repeatedly carrying out pivotal condensations of these two kinds one may arrive at the formula

$$\ln D_{N',N}(a_{-N'}, \ldots, a_N) = \ln\left(a_0 - \frac{t_{01} t_{10}}{a'_1} - \frac{t_{0,-1} t_{-1,0}}{a'_{-1}} \right) + \sum_{i=1}^{N} \ln a'_i + \sum_{i=1}^{N'} \ln a'_{-i} , \tag{A7}$$

where the a'_i are defined by the recurrence relations

$$a'_i = \begin{cases} a_i - \dfrac{t_{i,i+1} t_{i+1,i}}{a'_{i+1}} & \text{if } i \geqslant 1 \\ a_i - \dfrac{t_{i,i-1} t_{i-1,i}}{a'_{i-1}} & \text{if } i \leqslant -1 \end{cases} \tag{A8}$$

together with (A4) and (A5).

If one now substitutes $a_i = z - e_i$ in (A7), only the first term on the right depends upon e_0, so differentiating and using (A1)

$$g_{00}(z) = \left(z - e_0 - \frac{t_{01} t_{10}}{a'_1} - \frac{t_{0,-1} t_{-1,0}}{a'_{-1}} \right)^{-1} . \tag{A9}$$

If one now lets $N, N' \to \infty$ the quantities $1/a'_i$ pass over into the quantities δ_i satisfying (22) and (23) [which are equivalent to (A8)], and (A9) becomes (21).

Again from the definition (18) and the rule for differentiating determinants one may obtain (45). Equation (48) is obtained by simply stopping the repeated pivotal condensations which led to (A7) one step (on each side) before the last step, and then letting $N, N' \to \infty$: X in (48) represents the sums in (A7) but now taken from $i = 2$ to $i = N$ or N', so X does not depend upon t_{01}. Equation (50) is obtained by introducing an additional element x into $D_{N',N}$ at the (2,0) position, so that differentiation with respect to x will generate g_{20}, and then stopping the pivotal condensations at the point which gave (48).

These manipulations are made possible by the fact that $D_{N',N}$ is a tridiagonal matrix, which in turn is a consequence of the assumption that only nearest-neighbor transfer integrals need be considered. If one included next-nearest-neighbor transfer integrals, one would obtain instead a determinant with five nonvanishing diagonals. One could reduce its size in the same way by pivotal condensation, but would now obtain recurrence relations for the new elements of the middle three diagonals, and consequently much more complicated formulas.

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