large effects on anomalously transmitted intensities, and similar results were found for irradiated copper.[3] When defects are clustered, changes in the x-ray-diffraction properties are produced with a relatively small number of point defects. In fact, diffuse x-ray-scattering measurements as those presented here would appear to be valuable in determining whether isolated point defects had, in fact, clustered after some treatment. These results as well as those obtained previously using anomalous x-ray transmission should be less ambiguous than electrical resistivity or lattice-parameter measurements, and a comparison with measurements of other physical properties would appear to be very useful in determining, for example, if clustering were important in low-temperature annealing stages. Such experiments are now being planned for some of these crystals.

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[1] W. Cochran and G. Kartha, Acta Cryst. 9, 941 (1956).

[2] R. G. Perret and D. T. Keating, in *Small Angle X-Ray Scattering*, edited by H. Brumberger (Gordon and Breach, New York, 1967), p. 373.

[3] T. O. Baldwin, F. A. Sherrill, and F. W. Young, Jr., J. Appl. Phys. 39, 1541 (1968).

[4] R. Colella and A. Merlini, Phys. Status Solidi 14, 81 (1966).

[5] H. Peisl, H. Spalt, and W. Waidelich, Phys. Status Solidi. 23, K75 (1967).

[6] S. R. Austerman and K. T. Miller, Phys. Status. Solidi 11, 241 (1965).

[7] R. O. Simmons and R. W. Balluffi, J. Appl. Phys. 30, 1249 (1959).

[8] H. Ekstein, Phys. Rev. 68, 120 (1945).

[9] K. Huang, Proc. Roy. Soc. (London) A190, 122 (1947).

[10] M. A. Krivoglaz and K. P. Ryaboshapka, Phys. Metals Metallog. 15, 14 (1963).

[11] P. H. Dederichs (unpublished).

[12] F. W. Young, Jr., T. O. Baldwin, and P. H. Dederichs, in *International Conference on Vacancies and Interstitials in Metals*, edited by D. Schumacher (North-Holland, Amsterdam, 1968), Vol. II, p. 619.

[13] R. W. James, *Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1958).

[14] J. C. Crump, III (unpublished).

[15] B. H. Batterman, Appl. Phys. Letters 1, 68 (1962); Phys. Rev. 133, A759 (1964).

[16] S. Annaka *et al.*, J. Phys. Soc. Japan 21, 1559 (1966); 23, 372 (1967); 24, 1332 (1968).

[17] K. J. Bachmann, T. O. Baldwin, and F. W. Young, Jr., J. Appl. Phys. 41, 4783 (1970).

[18] J. R. Patel and B. W. Batterman, J. Appl. Phys. 39, 1541 (1968).

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Electronic Structure of Disordered Systems

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A method of calculating the electronic density of states in a disordered system is discussed. The case of bound bands is considered in detail. By a transformation of the overlap integral in the tight-binding theory, the Matsubara-Toyozawa and Matsubara-Kaneyoshi methods for calculating the electronic density of states is extended to topologically disordered systems. The same transformation is also applied to the band propagator expansion.

I. INTRODUCTION

In recent years, the problem of the effects of lattice disorder on the electronic density of states has been studied extensively.[1] The various techniques employed may be classified according to the types of disorder and the range of the electronic energy. It is customary to divide the electronic energy into two regions, the bound bands and the "free," or conduction, bands. As to the types of disorder, we shall follow Ziman[2] and classify them according to structural disorder (the loss of spatial periodicity in the arrangement of the lattice sites), and cellular disorder (the lack of periodicity of the atomic potential from cell to cell in an otherwise periodic lattice).

The problem of cellular disorder is better understood than the problem of structural disorder because the presence of a periodic lattice simplifies the problem considerably. At present, many sophisticated techniques for finding the electronic density of states in systems with cellular disorder have been developed and applied with considerable success to the problems of alloys.[3] The case of structural disorder on the other hand has not received the same attention since discussed in the works of Edwards[4] and Beeby and Edwards.[5] Edwards[4] showed that in the case of "free" bands and structural disorder, the density of states can be understood qualitatively from a perturbation expansion of the self-energy correction in the average Green's function of the electron. Recently Ziman[6] reviewed Edwards's work and pointed out that the summation of the perturbation series considered by Edwards must be carried to higher-order terms in order to produce the known band gaps even in a coarsely polycrystalline specimen. The case of structural disorder and bound bands is even less well understood. Although much has been learned by studying one-dimensional disordered systems, very little is known about three-dimensional systems. Some insight into this problem has been provided by the work of Beeby and Edwards.[5] They extend their calculations from free bands to bound bands by replacing the scattering potential by a t matrix.

As is well known, this leads to restricted sums in the t-matrix expansion of the Green's function. In order to perform the summation, Beeby and Edwards introduced what they called the "geometric' approximation," i.e., they treated the t-matrix expansion as if it were a geometric series. The corrections to the approximation are however difficult to treat in this case. A similar problem occurs in the case of cellular disorder. There the treatment is not complicated by lattice disorder and considerable progress has been achieved in calculating the correction terms. In view of this progress it would seem advantageous if we could carry over the techniques developed for systems with cellular disorder to systems with structural disorder. However, this program quickly runs into difficulty because of the lack of a Fourier transform commonly used in such cases. In this paper we shall apply a transformation first used by Wu and Taylor[7] in their work on the lattice dynamics of disordered alloys and glasses to the problem of the electronic density of states. We shall show that by this method, most of the techniques developed for cellular disorder can be carried over to the problem of structural disorder. In Sec. II, we shall formulate the problem in the tight-binding case and in Sec. III, we shall develop the Wu-Taylor transformation for band structure calculations. The application of the transformation to the locator expansion of the Green's function will be treated in Sec. IV and the application to band-propagator expansion, in Sec. V.

II. FORMULATION OF THE PROBLEM

In order to simplify the discussion of the effects of structural disorder on the electronic density of states, we shall use the one electron theory with the Hamiltonian

$$H = p^2/2m + \sum_{\vec{l}} v(\vec{r} - \vec{l}), \tag{2.1}$$

where $\vec{l}$ denotes the atomic sites and $v(\vec{r} - \vec{l})$ denotes the interaction potential due to the atom at site $\vec{l}$. We are mainly concerned with the effects of the disordering of the sites on the bound bands. The wave function is expanded in terms of the atomic orbitals

$$\psi = \sum_{\vec{l}} \alpha_{\vec{l}} \Phi_{\vec{l}}, \tag{2.2}$$

where for simplicity we assume as in the Anderson model[8] that each atom has a single bound state. The equation of motion for the coefficients $\alpha_{\vec{l}}$ is

$$i \dot{\alpha}_{\vec{l}} = \sum_{\vec{l}} H_{\vec{l}\vec{l}'} \alpha_{\vec{l}'}. \tag{2.3}$$

The matrix element $H_{\vec{l}\vec{l}'}$ is given by

$$H_{\vec{l}\vec{l}'} = w_{\vec{l}} \delta_{\vec{l}\vec{l}'} + V_{\vec{l}\vec{l}'}, \tag{2.4}$$

where $w_{\vec{l}}$ is the bound-state energy and $V_{\vec{l}\vec{l}'}$ is the transfer integral

$$V_{\vec{l}\vec{l}'} \equiv (\Phi_{\vec{l}}, \sum_{\vec{l}'' \neq \vec{l}} v(\vec{r} - \vec{l}'')\Phi_{\vec{l}'}) . \tag{2.5}$$

The density of states for the electrons $\rho(\vec{l}, \epsilon)$ can be derived from the Green's function of Eq. (2.3)

$$\sum_{\vec{l}''} (z\, \delta_{\vec{l}\vec{l}''} - H_{\vec{l}\vec{l}''}) G_{\vec{l}''\vec{l}'}(z) = \delta_{\vec{l}\vec{l}'}, \tag{2.6}$$

$$\rho(\vec{l}, \epsilon) = -\pi^{-1} \operatorname{Im} G_{\vec{l}\vec{l}}(z \to \epsilon + i0). \tag{2.7}$$

Equation (2.6) can be written simply in operator form

$$G = G_0 + G_0 H G, \tag{2.8}$$

where

$$G_0(z) = z^{-1} I,$$

I being the unit matrix. The problem of calculating G is then usually reduced to the summation of the iterative solution of Eq. (2.8):

$$G=G_0+G_0HG_0+G_0HG_0HG_0+\cdots. \tag{2.9}$$

III. TRANSFORMATION OF H

The solution of Eq. (2.8) can be greatly simplified by a judicious choice of the transformation S of G, such that

$$\tilde{G}\equiv S^{-1}GS,$$

with $\tilde{G}$ satisfying

$$\tilde{G}=G_0+G_0(S^{-1}HS)\tilde{G}\ . \tag{3.1}$$

For a periodic lattice, the transformation best suited is the matrix

$$S_{\vec{l}\vec{k}}=\sqrt{N}^{-1}\,e^{-i\vec{k}\cdot\vec{l}}, \tag{3.2}$$

with its inverse

$$E_{\vec{k}\vec{l}}=\sqrt{N}^{-1}e^{i\vec{k}\cdot\vec{l}}\ , \tag{3.3}$$

where $\vec{k}$ is defined to lie within the first Brillouin zone and to satisfy periodic boundary condition.

For a structurally disordered system, E is no longer the inverse of S, and in addition, there is no obvious Brillouin zone to limit the sum over $\vec{k}$. Therefore, if we wish to retain S as our transformation, these two difficulties have to be overcome. This can be accomplished by adopting the method introduced by Wu and Taylor[7] in which the inverse of S is written as

$$(I+R)S^{-1}=E. \tag{3.4}$$

Multiplication on the right by S and using the definitions of S and E then give the matrix element of R:

$$R_{\vec{k}\vec{k}'}=N^{-1}\textstyle\sum_{\vec{l}}\,e^{i(\vec{k}-\vec{k}')\cdot\vec{l}}-\delta_{\vec{k}\vec{k}'}\ . \tag{3.5}$$

The matrix element $(I+R)_{\vec{k}\vec{k}'}$ is simply related to the structure factor of the solid; in a perfectly ordered crystal, it is $\delta_{\vec{k},\vec{k}+\vec{K}}$, where $\vec{K}$ is a reciprocal lattice vector. For a disordered system, the function $\delta_{\vec{k},\vec{k}+\vec{K}}$ is broadened but x-ray and neutron diffraction studies of many amorphous materials have shown that a strong peak remains. Thus, in the computation of the sum over $\vec{k}$ one finds that a natural cutoff is built-in in the factors $(I+R)_{\vec{k}\vec{k}'}$, although it is not as sharp as in the perfectly ordered case.[7]

Using the transformations S and S^{-1} described, we find that

$$(S^{-1}HS)_{\vec{k}\vec{k}'}=\frac{1}{N}\sum_{\vec{k}''}\left(\frac{1}{I+R}\right)_{\vec{k}\vec{k}''}\sum_{\vec{l}}e^{i(\vec{k}''-\vec{k}')\cdot\vec{l}}$$
$$\times\sum_{\vec{L}}H_{\vec{l},\vec{l}-\vec{L}}\,e^{i\vec{k}'\cdot\vec{L}}\ . \tag{3.6}$$

As expected, (3.6) cannot be separated into a structural and a scattering part. However, for the purpose of generating a perturbation or self-consistent type of calculation, we shall decompose the last summation in (3.6) into

$$\textstyle\sum_{\vec{L}}H_{\vec{l},\vec{l}-\vec{L}}\,e^{i\vec{k}'\cdot\vec{L}}=\tilde{V}(\vec{k}')+U(\vec{l},\vec{k}'), \tag{3.7}$$

where $\tilde{V}(\vec{k}')$ can either be chosen to approximate as best as possible the average motion of the electron in the potential field or calculated self-consistently. For example, for systems which exhibit short-range order, we may choose $\tilde{V}(\vec{k}')$ to be

$$\tilde{V}(\vec{k}')=N^{-1}\textstyle\sum_{\vec{l}}\int d\vec{R}\,H_{\vec{l},\vec{l}-\vec{R}}\,g(\vec{R})\,e^{i\vec{k}'\cdot\vec{R}}, \tag{3.8}$$

where $g(\vec{R})$ is the pair correlation function. This choice describes a model which in the limit of large short-range order distances approaches the microcrystalline model.

For convenience in later analysis, we shall define the operators $\tilde{V}$ and $\tilde{W}$ so that

$$S^{-1}HS\equiv\tilde{H}=\tilde{V}+\tilde{W}, \tag{3.9}$$

where $\tilde{V}$ and $\tilde{W}$ have matrix elements

$$(\tilde{V})_{\vec{k}\vec{k}'}=\tilde{V}(\vec{k})\delta_{\vec{k}\vec{k}'}\ , \tag{3.10}$$

$$(\tilde{W})_{\vec{k}\vec{k}'}=\frac{1}{N}\sum_{\vec{k}''}\left(\frac{1}{1+R}\right)_{\vec{k}\vec{k}''}\sum_{\vec{l}}e^{i(\vec{k}''-\vec{k}')\cdot\vec{l}}\,U(\vec{l},\vec{k}')$$
$$=\sum_{\vec{l}}S^{-1}_{\vec{k}\vec{k}}\,U(\vec{l},\vec{k})\,S_{\vec{l}\vec{k}}\ . \tag{3.11}$$

IV. LOCATOR EXPANSION

In this section we describe how one can calculate $\tilde{G}$ by generalizing the locator expansion method introduced by Matsubara and Toyozawa,[9] by Matsubara and Kaneyoshi,[10] and the cumulant summation of the expansion by Yonezawa and Matsubara,[11] briefly the MTKY method. A comprehensive review of the method can be found in a recent paper by Ziman,[3] and our generalization follows closely the outline of the method as presented in that paper.

The locator expansion of $\tilde{G}$ is given by

$$\tilde{G}=\tilde{\sigma}+\tilde{\sigma}\tilde{V}\tilde{\sigma}+\tilde{\sigma}\tilde{V}\tilde{\sigma}\tilde{V}\tilde{\sigma}+\cdots, \tag{4.1}$$

where

$$\tilde{\sigma}=\frac{1}{\epsilon}+\frac{1}{\epsilon}\tilde{W}\frac{1}{\epsilon}+\frac{1}{\epsilon}\tilde{W}\frac{1}{\epsilon}\tilde{W}\frac{1}{\epsilon}+\cdots. \tag{4.2}$$

In the case of cellular disorder, we have

$$R=0,$$

$$U(\vec{l},\vec{k}')=w_{\vec{l}}\ ,$$

$$\tilde{W}_{\vec{k}\vec{k}'}=N^{-1}\textstyle\sum_{\vec{l}}e^{i(\vec{k}-\vec{k}')\cdot\vec{l}}\,w_{\vec{l}},$$

and hence

$$\tilde{\sigma}_{\vec{k}\vec{k}'}=N^{-1}\textstyle\sum_{\vec{l}}(\epsilon-w_{\vec{l}})^{-1}e^{i(\vec{k}-\vec{k}')\cdot\vec{l}}\ . \tag{4.3}$$

The quantity

$$\sigma_{\vec{l}} \equiv (\epsilon - w_{\vec{l}})^{-1} \tag{4.4}$$

is called the locator in the MTKY formulation, and (4.3) is its Fourier transform. For systems with structural disorder, we generalize (4.3) by

$$\tilde{\sigma}_{\vec{k}\vec{k}'} = \sum_{\vec{l}} S^{-1}_{\vec{k}\vec{l}}\, \sigma_{\vec{l}\vec{l}'} S_{\vec{l}'\vec{k}'}, \tag{4.5}$$

or simply

$$\tilde{\sigma} = S^{-1} \sigma S . \tag{4.6}$$

The generalized locator σ can be determined from (4.6) and (4.2)

$$\begin{aligned} \sigma &= S \tilde{\sigma} S^{-1} \\ &= \frac{1}{\epsilon} + \frac{1}{\epsilon} S \tilde{W} S^{-1} \frac{1}{\epsilon} + \frac{1}{\epsilon} S \tilde{W} S^{-1} \frac{1}{\epsilon} + \cdots \\ &= (\epsilon - w)^{-1}, \end{aligned} \tag{4.7}$$

where

$$w \equiv S \tilde{W} S^{-1} \tag{4.8}$$

or

$$\begin{aligned} w_{\vec{l}\vec{l}'} &= \sum_{\vec{k}\vec{k}'} S_{\vec{l}\vec{k}} \tilde{W}_{\vec{k}\vec{k}'} S^{-1}_{\vec{k}'\vec{l}'} \\ &= \sum_{\vec{k}\vec{k}'} S_{\vec{l}\vec{k}} \left(\sum_{\vec{l}''} S^{-1}_{\vec{k}\vec{l}''} U(\vec{l}'' \vec{k}') S_{\vec{l}''\vec{k}'} \right) \\ &= \sum_{\vec{k}'} U(\vec{l}, \vec{k}') S_{\vec{l}\vec{k}'} S^{-1}_{\vec{k}'\vec{l}'} . \end{aligned} \tag{4.9}$$

In the case of cellular disorder, $U(\vec{l}, \vec{k}')$ is independent of $\vec{k}'$ $[U(\vec{l}, \vec{k}') = w_{\vec{l}}]$, so that (4.9) becomes

$$w_{\vec{l}\vec{l}'} = w_{\vec{l}} \delta_{\vec{l}\vec{l}'},$$

$$\sigma_{\vec{l}\vec{l}'} = \sigma_{\vec{l}} \delta_{\vec{l}\vec{l}'},$$

where $\sigma_{\vec{l}}$ is simply the MTKY locator $(\epsilon - w_{\vec{l}})^{-1}$. The success of the MTKY method depends on the diagonalization of σ, i.e., the local propagation of an electron from site $\vec{l}$ back to $\vec{l}$, the propagation from $\vec{l}$ to $\vec{l}'$ being accounted for completely by the Fourier transform of the transfer integrals. For systems with structural disorder, σ is no longer diagonal and the fluctuations in local potential also contribute to the transfer of electrons. The extent to which the nondiagonal part of σ contributes to the transfer depends on the choice of $\tilde{V}$ because the magnitude and $\vec{k}'$ dependence of $U(\vec{l}, \vec{k}')$ depend entirely on the same, as can be seen by rearranging (3.7)

$$U(\vec{l}, \vec{k}') = \sum_{\vec{L}} H_{\vec{l},\vec{l}-\vec{L}}\, e^{i\vec{k}' \cdot \vec{L}} - \tilde{V}(\vec{k}') .$$

Thus, if $\tilde{V}(\vec{k}')$ were selected to approximate as best as possible the average motion of the electrons, the contributions from the nondiagonal elements of σ will be small; their contributions becoming zero in the limit of cellular disorder when $\tilde{V}(\vec{k}')$ is chosen to be the Fourier transform of the transfer integral. It is known[3] that for systems with cellular disorder, the behavior of $\sigma_{\vec{l}}$ plays an essential role in determining the localization of electrons. We thus expect the diagonality condition in σ to play a similar role in systems that are structurally disordered as well. In fact we shall show that if σ has a large diagonal part, it is possible to reduce the problem into a form similar to the case of cellular disorder. In order to do this, we formally decompose σ into a diagonal and nondiagonal part,

$$\sigma = \sigma_{\mathrm{d}} + \sigma_{\mathrm{nd}} . \tag{4.10}$$

This decomposition can always be done. Here, we choose σ_d and σ_{nd}, such that

$$(\sigma_{\mathrm{d}})_{\vec{l}\vec{l}'} = \sigma_{\vec{l}\vec{l}} \delta_{\vec{l}\vec{l}'} ,$$

$$(\sigma_{\mathrm{nd}})_{\vec{l}\vec{l}'} = \sigma_{\vec{l}\vec{l}'} (1 - \delta_{\vec{l}\vec{l}'}).$$

In order to make the diagonal elements of σ_d similar in form to the MTKY locator, we also decompose w into a diagonal and nondiagonal part in the following way:

$$(w_{\mathrm{d}})_{\vec{l}\vec{l}'} \equiv \bar{w}_{\vec{l}} \delta_{\vec{l}\vec{l}'} ,$$

where

$$\bar{w}_{\vec{l}} \equiv \sum_{\vec{k}} U(\vec{l}, \vec{k}) S_{\vec{l}\vec{k}} S^{-1}_{\vec{k}\vec{l}} . \tag{4.11}$$

The generalized locator (4.7) can now be written as

$$\sigma = (\epsilon - w_{\mathrm{d}} - \delta w)^{-1} , \tag{4.12}$$

where

$$\delta w = w - w_{\mathrm{d}} ,$$

$$(\delta w)_{\vec{l}\vec{l}'} = \sum_{\vec{k}} U(\vec{l}, \vec{k}) S_{\vec{l}\vec{k}} (S^{-1}_{\vec{k}\vec{l}'} - S^{-1}_{\vec{k}\vec{l}} \delta_{\vec{l}\vec{l}'}) . \tag{4.13}$$

Expanding (4.12) in terms of

$$\sigma^{(0)} \equiv (\epsilon - w_{\mathrm{d}})^{-1} \tag{4.14}$$

we get

$$\sigma = \sigma^{(0)} + \sigma^{(0)} \delta w \sigma^{(0)} + \sigma^{(0)} \delta w \sigma^{(0)} \delta w \sigma^{(0)} + \cdots . \tag{4.15}$$

We can introduce a diagrammatic scheme for summing (4.15):

(a) Define the matrix elements of $\sigma^{(0)}$ by

$$\sigma^{(0)}_{\vec{l}\vec{l}'} \equiv \sigma^{(0)}_{\vec{l}} \delta_{\vec{l}\vec{l}'} ,$$

where

$$\sigma^{(0)}_{\vec{l}} \equiv (\epsilon - \bar{w}_{\vec{l}})^{-1} ,$$

and denote it by a loop, Fig. 1(a).

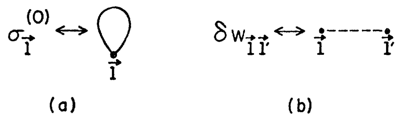

FIG. 1. Diagrammatic representations of $\sigma^{(0)}_{\vec{l}}$ and $\delta w_{\vec{l}\vec{l}'}$.

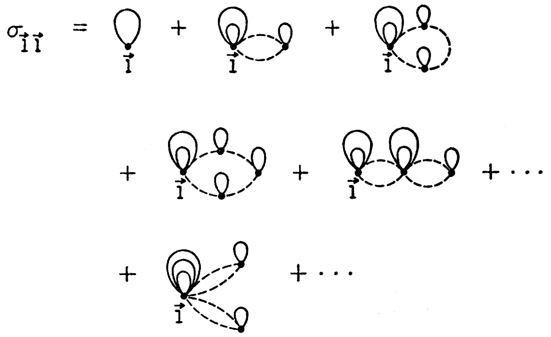

FIG. 2. Diagrammatic representation of $\sigma_{\vec{l}\vec{l}}$.

(b) Define the matrix elements of δw, i.e., $(\delta w)_{\vec{l}\vec{l}'}$, by a dashed line between $\vec{l}$ and $\vec{l}'$, Fig. 1(b).

In this way, the diagonal elements of σ will be represented by those diagrams which cannot be split into two parts by cutting only one dashed line, i.e., as in Fig. 2, where all the loops not labeled by $\vec{l}$ should be summed over all sites except $\vec{l}$. The expansion (Fig. 2) is evidently a power series in $\sigma_{\vec{l}}^{(0)}$, as can be shown by collecting terms with one loop at $\vec{l}$, two loops at $\vec{l}$, etc. A simple calculation shows that

$$\sigma_{\vec{l}\vec{l}}=\sigma_{\vec{l}}^{(0)}+\Omega_{\vec{l}}(\sigma_{\vec{l}}^{(0)})^2+\Omega_{\vec{l}}^2(\sigma_{\vec{l}}^{(0)})^3+\cdots , \qquad (4.16)$$

where $\Omega_{\vec{l}}$ is represented schematically by Fig. 3.

Summing (4.16), we get

$$\sigma_{\vec{l}\vec{l}}=(1-\Omega_{\vec{l}}\sigma_{\vec{l}}^{(0)})^{-1}\sigma_{\vec{l}}^{(0)}$$
$$=(\epsilon-\overline{w}_{\vec{l}}-\Omega_{\vec{l}})^{-1} , \qquad (4.17)$$

which is similar in form to the MTKY locator except that $w_{\vec{l}}$ is now $\overline{w}_{\vec{l}}+\Omega_{\vec{l}}$. Looking back at the expression (4.11) for $\overline{w}_{\vec{l}}$, we see that it corresponds to the local potential in the case of cellular disorder, except for the fact that the extra structural factor $S_{\vec{l}\vec{k}}S_{\vec{k}\vec{l}}^{-1}$ is needed to define it. The additional term $\Omega_{\vec{l}}$ can be thought of as a shift in the local potential at $\vec{l}$ arising from the correlation with all the local potentials at other sites. This is a feature which has not been treated until now.

We shall finally show that by neglecting the nondiagonal part of σ one can reduce the problem into a cellular disorder problem. Even with a diagonal σ the problem remains difficult because instead of the Fourier transform of the locator (4.3), we have

$$\vec{\sigma}_{\vec{k}\vec{k}'}=\sum\nolimits_{\vec{l}}S_{\vec{k}\vec{l}}^{-1}\overline{\sigma}_{\vec{l}}S_{\vec{l}\vec{k}'} , \qquad (4.18)$$

where for convenience, we define

$$(\sigma_d)_{\vec{l}\vec{l}}\equiv\sigma_{\vec{l}\vec{l}}\equiv\overline{\sigma}_{\vec{l}} . \qquad (4.19)$$

To illustrate the difficulties, we examine the terms in the locator expansion of the ensemble-averaged $\langle\tilde{G}_{\vec{k}\vec{k}'}\rangle$. Consider a third-order contribution containing two identical sites $\vec{l}$ and a third different site $\vec{l}'$. The contribution would then have the form

$$\frac{1}{N^3}\sum_{\vec{l}\vec{l}'\vec{k}''}\sum_{\vec{k}'''}\langle(S_{\vec{k}\vec{l}}^{-1}\overline{\sigma}_{\vec{l}}S_{\vec{l}\vec{k}''})\tilde{V}_{\vec{k}''}(S_{\vec{k}''\vec{l}}^{-1}\overline{\sigma}_{\vec{l}}S_{\vec{l}\vec{k}'''})\tilde{V}_{\vec{k}'''}(S_{\vec{k}'''\vec{l}'}^{-1}\overline{\sigma}_{\vec{l}'}S_{\vec{l}'\vec{k}})\rangle$$

$$=\frac{1}{N^3}\sum_{\vec{l}\vec{l}'}\sum_{\vec{k}''\vec{k}'''}\sum_{\vec{q}\vec{q}'\vec{q}''}\left\langle\left(\frac{1}{I+R}\right)_{\vec{k}\vec{q}}e^{i(\vec{q}-\vec{k}'')\cdot\vec{l}}\left(\frac{1}{I+R}\right)_{\vec{k}''\vec{q}'}e^{i(\vec{q}'-\vec{k}''')\cdot\vec{l}}\right.$$

$$\left.\times\left(\frac{1}{I+R}\right)_{\vec{k}'''\vec{q}''}e^{i(\vec{q}''-\vec{k})\cdot\vec{l}'}\tilde{V}_{\vec{k}''}\tilde{V}_{\vec{k}'''}\overline{\sigma}_{\vec{l}}^2\overline{\sigma}_{\vec{l}'}\right\rangle . \qquad (4.20)$$

From Eq. (4.20), it is obvious that structural disorder prevents the collapse of the exponential factors by introducing the intervening matrix elements of $(1+R)^{-1}$. However, considerable simplifications occur when the $\overline{\sigma}_{\vec{l}}$'s vary slowly over $\vec{l}$ because then we can move $\langle\overline{\sigma}_{\vec{l}}^2\overline{\sigma}_{\vec{l}'}\rangle$ out of the summation over $\vec{l}$ and $\vec{l}'$. The summation over $\vec{l}'$ and $\vec{q}''$ gives

$$\frac{1}{N}\sum_{\vec{l}'\vec{q}''}\left(\frac{1}{1+R}\right)_{\vec{k}'''\vec{q}}e^{i(\vec{q}''-\vec{k})\cdot\vec{l}}=\delta_{\vec{k}''',\vec{k}} ,$$

and the summation over $\vec{l}$ and $\vec{q}$, $\vec{q}'$ gives

$$\frac{1}{N^2}\sum_{\vec{l},\vec{q},\vec{q}'}\left(\frac{1}{1+R}\right)_{\vec{k}\vec{q}}e^{i(\vec{q}-\vec{k}''+\vec{q}'-\vec{k})\cdot\vec{l}}\left(\frac{1}{1+R}\right)_{\vec{k}'',\vec{q}'}$$

$$=\sum_{\vec{q}'}\delta_{\vec{k},\vec{k}''-\vec{q}'+\vec{k}}\left(\frac{1}{1+R}\right)_{\vec{k}'',\vec{q}'}$$

$$=\left(\frac{1}{1+R}\right)_{\vec{k}'',\vec{k}''} .$$

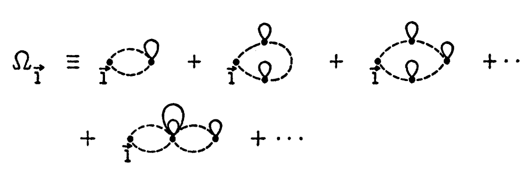

FIG. 3. Diagrammatic representation of $\Omega_{\vec{l}}$.

Therefore, (4.20) becomes

$$\overline{V}\,\tilde{V}_{\vec{k}}\langle\overline{\sigma}^{2}_{\vec{l}}\overline{\sigma}_{\vec{l}'}\rangle\ ,$$

where

$$\overline{V}\equiv\sum_{\vec{k}''}\left(\frac{1}{1+R}\right)_{\vec{k}''\vec{k}''}\tilde{V}_{\vec{k}''}\ , \tag{4.21}$$

which is similar to the result of the MTKY method when applied to a system with cellular disorder, except that here $\overline{V}$ is given by (4.21) instead of $N^{-1}\sum_{\vec{k}}V_{\vec{k}}$. We see that the reduction into the case of cellular disorder involves the assumptions of the smallness of the nondiagonal elements of σ and the slow variation of the diagonal elements $\overline{\sigma}_{\vec{l}}$. Both assumptions are approximately true for most physical systems and the approximation can be improved by proper choices of $\tilde{V}$. The result of the reduction is the redefinition of $\sigma_{\vec{l}}$ by (4.17) and $\overline{V}$ by (4.23).

V. BAND PROPAGATOR EXPANSION

The transformation discussed in Secs. II and III can also be applied to the band propagator expansion of $\tilde{G}$. The part of $\tilde{H}$ which is diagonal in $\vec{k}$, i.e., $\tilde{V}$, serves naturally for defining a band propagator:

$$\mathcal{G}(z)=(z-\tilde{V})^{-1}\ . \tag{5.1}$$

The band propagator expansion of $\tilde{G}$ is then

$$\tilde{G}=\mathcal{G}+\mathcal{G}\tilde{W}\mathcal{G}+\mathcal{G}\tilde{W}\mathcal{G}\tilde{W}\mathcal{G}+\cdots\ . \tag{5.2}$$

The ensemble-average $\tilde{G}$ can be evaluated by summing Eq. (5.2) directly. It can also be calculated by applying a self-consistent scheme such as the one due to Velický, Kirkpatrick, and Ehrenreich[12] (VKE). The direct summation can be done by defining the "proper self-energy" part $\Sigma(\mathcal{K}, z)$, where

$$\begin{aligned}\Sigma(\vec{k}, z)\equiv\tilde{W}_{\vec{k}\vec{k}}&+\sum_{\vec{k}'\neq\vec{k}}\tilde{W}_{\vec{k}\vec{k}'}\mathcal{G}(\vec{k}', z)\tilde{W}_{\vec{k}'\vec{k}}\\&+\sum_{\vec{k}',\vec{k}''\neq\vec{k}}\tilde{W}_{\vec{k}\vec{k}'}\mathcal{G}(\vec{k}', z)\tilde{W}_{\vec{k}'\vec{k}''}\\&\times\mathcal{G}(\vec{k}'', z)\tilde{W}_{\vec{k}''\vec{k}}+\cdots\ .\end{aligned} \tag{5.3}$$

Then we have

$$\langle\tilde{G}(\vec{k}, z)\rangle=\langle[z-\tilde{V}(\vec{k})-\Sigma(\vec{k}, z)]^{-1}\rangle\ . \tag{5.4}$$

The essential feature of $\Sigma(\vec{k}, z)$, which distinguishes it from the case of perfect lattice, is the appearance of the structural factors contained in the $\tilde{W}$'s. The degree to which effects of structural disorder is important in determining band structure can then be investigated by studying Eq. (5.3).

The average Green's function (5.4) can also be calculated self-consistently. For simplicity, we follow the elegant formulation by Velický, Kirkpatrick, and Ehrenreich.[12] We shall adopt their notation to the extent possible. The self-consistent approach involves the derivation of an effective Hamiltonian which is defined by the equation

$$\langle G\rangle\equiv(z-H_{\text{eff}})^{-1}\ . \tag{5.5}$$

The calculation starts by selecting as good an approximation K to H_{eff} as possible and defining in terms of K a T matrix by

$$G=\mathcal{G}+\mathcal{G}T\mathcal{G}\ , \tag{5.6}$$

where

$$\mathcal{G}\equiv(z-K)^{-1}\ .$$

In terms of T and $\mathcal{G}$, VKE found that

$$H_{\text{eff}}=K+\langle T\rangle(1+\mathcal{G}\langle T\rangle)^{-1}\ . \tag{5.7}$$

A self-consistent scheme can then be generated by requiring that $\langle T[K]\rangle=0$. In actual calculations, the propagator $\mathcal{G}$ is usually chosen to approximate the band structure as best as possible. This requires the knowledge of some band structure beforehand and the commonly chosen one is the perfectly ordered lattice band structure. The calculation is then vastly facilitated by the existence of a Fourier transform for the approximated band propagator. The limitation of this perfect lattice type of theory is that it will be quite difficult to find a periodic lattice which approximates amorphous materials. This can be easily removed if we work with the transformed Hamiltonian $\tilde{H}=\tilde{V}+\tilde{W}$. The natural choice of $\tilde{K}$ would then be $\tilde{V}$, and $\mathcal{G}$ will be the same as (5.1). The operator

$$\tilde{H}-\tilde{K}\equiv\sum\nolimits_{\vec{l}}V_{\vec{l}}\ , \tag{5.8}$$

which is needed in VKE for calculating T, becomes

$$\tilde{H}-\tilde{K}=\tilde{W}\ , \tag{5.9}$$

from which we find the matrix element of $V_{\vec{l}}$ to be

$$V_{\vec{l}}(\vec{k}, \vec{k}')=S^{-1}_{\vec{k}\vec{l}}U(\vec{l}, \vec{k}')S_{\vec{l}\vec{k}'}\ . \tag{5.10}$$

The scattering from individual sites is then given by the potential $U(\vec{l}, \vec{k}')$ which is due to fluctuation from local order. For cellularly disordered system, $V_{\vec{l}}(\vec{k}, \vec{k}')$ reduces to $w_{\vec{l}}e^{i(\vec{k}-\vec{k}')\cdot\vec{l}}$.

$V_{\vec{l}}(\vec{k}, \vec{k}')$ as given by (5.10) permits the matrix element of the T matrix associated with site $\vec{l}$

$$T_{\vec{l}}\equiv(1-V_{\vec{l}}\mathcal{G})^{-1}V_{\vec{l}} \tag{5.11}$$

to be summed analytically. To do this, we substitute the definitions of $S^{-1}_{\vec{k}\vec{l}}$ and $S_{\vec{l}\vec{k}'}$ into (5.10) to get

$$V_{\vec{l}}(\vec{k}, \vec{k}')=\sum_{\vec{k}''}\left(\frac{1}{1+R}\right)_{\vec{k}\vec{k}''}e^{i(\vec{k}''\vec{k}')\cdot\vec{l}}\,U(\vec{l}, \vec{k}')\ ; \tag{5.12}$$

then defining

$$J(\vec{l}, \vec{k})=\sum_{\vec{k}''}\left(\frac{1}{1+R}\right)_{\vec{k}\vec{k}''}e^{i(\vec{k}''-\vec{k})\cdot\vec{l}}\ , \tag{5.13}$$

we rewrite (5.12) as

$$V_{\vec{1}}(\vec{k}, \vec{k}')\, e^{i(\vec{k}-\vec{k}')\cdot\vec{1}} J(\vec{1}, \vec{k}) U(\vec{1}, \vec{k}') \,. \tag{5.14}$$

Note that the factor $J(\vec{1}, \vec{k})$ depends only on the structure of the lattice, and for $(1+R)^{-1}_{\vec{k}\vec{k}''}$ peaked at $\vec{k}''=\vec{k}$ this factor is essentially 1. The factorization of $V_{\vec{1}}(\vec{k}, \vec{k}')$ into a product of functions of $\vec{k}$ and $\vec{k}'$ makes it possible to sum (5.11):

$$\begin{aligned} T_{\vec{1}}(\vec{k}, \vec{k}') &= V_{\vec{1}}(\vec{k}, \vec{k}') + \sum_{\vec{k}''} V_{\vec{1}}(\vec{k}, \vec{k}'') \\ &\quad \times \mathcal{G}(\vec{k}'', z) V_{\vec{1}}(\vec{k}'', \vec{k}') + \cdots \\ &= e^{i(\vec{k}-\vec{k}')\cdot\vec{1}} \frac{J(\vec{1}, \vec{k}) U(\vec{1}, \vec{k}')}{1 - \sum_{\vec{k}} U(\vec{1}, \vec{k}) \mathcal{G}(\vec{k}, z) J(\vec{1}, \vec{k})} \,. \end{aligned} \tag{5.15}$$

Thus the effect of multiple scattering from a single site is to enhance the local scattering $V_{\vec{1}}(\vec{k}, \vec{k}')$ by a site depend factor $[1 - \sum_{\vec{k}} U(\vec{1}, \vec{k}) \mathcal{G}(\vec{k}, z) J(\vec{1}, \vec{k})]^{-1}$. After making the average effective wave approximation,[12] VKE were able to reduce (5.7) into

$$H_{\text{eff}} = K + \sum_{\vec{1}} \langle T_{\vec{1}} \rangle (1 + \mathcal{G} \langle T_{\vec{1}} \rangle)^{-1} \,. \tag{5.16}$$

As the matrix elements of $T_{\vec{1}}$ given in (5.15) are still in the factorized form, the matrix elements of $\langle T_{\vec{1}} \rangle (1+\mathcal{G}\langle T_{\vec{1}} \rangle)^{-1}$ in (5.16) can again be summed analytically. Thus the VKE method can be carried through without much complications from structural disorder. Although further analysis of the result will depend on the specific system or model ensembles, it is clear from this illustration that the present formulation would apply readily to the band-propagator method in general.

VI. DISCUSSION

In this paper, we have introduced a method for treating the problem of structural disorder in the calculation of the electronic density of states in disordered systems. The central point of the formulation is the application of the Wu-Taylor transformation to the Green's-function equation. This enables us to define a site-dependent scattering potential $U(\vec{1}, \vec{k})$. Using $U(\vec{1}, \vec{k})$ it is then possible to define a generalized locator in the case of the locator expansion and a T matrix in the case of the band-propagator expansion. However, use of the Wu-Taylor transformation also introduces structure-dependent factors of $(1+R)^{-1}$ into the expansions. These factors are of course to be expected. Fortunately they do not present any serious complication to the calculation. In fact, we have illustrated the applicability of the formulation by extending two known methods, the MTKY method and the VKE method, for systems with cellular disorder to systems with structural disorder. Although we presently place our emphasis on the formulation, the two cases considered were carried sufficiently far so that when applied to specific systems, obtainable results are clearly in sight. These results for one-dimensional as well as three-dimensional disordered systems will be discussed in a subsequent paper.

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[1] A comprehensive review and list of references can be found in N. F. Mott, Advan. Phys., 16, 49 (1967).

[2] J. M. Ziman, J. Phys. C 1, 1532 (1968).

[3] See, for example, J. M. Ziman, J. Phys. C. 2, 1230 (1969).

[4] S. F. Edwards, Proc. Roy. Soc. (London) A267, 518 (1962).

[5] J. Beeby and S. F. Edwards, Proc. Roy. Soc. (London) A274, 395 (1963).

[6] J. M. Ziman, J. Phys. C 2, 1704 (1969).

[7] S. Wu and P. L. Taylor, Bull. Am. Phys. Soc. 14, 427 (1969); also Phys. Rev. B 2, 1752 (1970).

[8] P. W. Anderson, Phys. Rev. 109, 1492 (1958).

[9] T. Matsubara and Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) 26, 739 (1961).

[10] T. Matsubara and T. Kaneyoshi, Progr. Theoret. Phys. (Kyoto) 36, 695 (1966).

[11] F. Yonezawa and T. Matsubara, Progr. Theoret. Phys. (Kyoto) 35, 759 (1966).

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