

electron-electron scattering—including those which do not result in spin flips.

Two conclusions may finally be drawn regarding the extent of agreement between theory and experiment for the resistivity. On the one hand, the semiquantitative agreement between the above theoretical and experimental expressions for $A(c)$ would suggest that the spin-fluctuation contribution to the low-temperature electrical resistivity of dilute Pt-Ni alloys is certainly significant and perhaps dominant. On the other hand, the factor-of-2 difference between the theoretical and experimental values for $(1/A)(dA/dc)$ may be viewed as at least qualitatively significant. In this case, the theory and experiment taken together are consistent

with the presence of an additional, concentration-independent contribution to the resistivity having the form $A'T^2$, where $A' \sim \frac{1}{2}[A(\text{Pt})]_{\text{expt}}$. A term of this type and magnitude might well arise from non-spin-flip (Baber) electron-electron scattering.

ACKNOWLEDGMENTS

The authors are grateful to O. Gates for wet-chemical analysis, E. J. Brooks and G. A. Picklo for x-ray fluorescence analysis, and S. H. Cress for spectrographic analysis of all the samples used in this study. We are also grateful to P. Lederer and D. L. Mills for stimulating and helpful discussions.

PHYSICAL REVIEW B

VOLUME 1, NUMBER 8

15 APRIL 1970

Electronic States in Liquid Metals: A Generalization of the Coherent-Potential Approximation for a System with Short-Range Order*

B. L. GYORFFY†

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 1 December 1969)

The problem of finding the ensemble averaged Green's function $\langle G \rangle$ which describes an electron moving in the potential field of N stationary scatterers is formulated in terms of multiple scattering theory. The correlations between the positions of the scatterers are explicitly taken into account. By making use of the quasicrystalline approximation and a generalization of the coherent-potential prescription, a procedure for calculating $\langle G \rangle$ is proposed. Because of the use of the quasicrystalline approximation, it involves only the radial distribution function of the scatterers in addition to the scatterer-electron interaction potential. It is shown that the procedure reduces to the coherent-potential approximation for randomly distributed scatterers, i.e., no short-range order, and to Korringa's band-structure calculation for an order lattice. It is pointed out that the method is applicable to the problem of electronic states in random alloys and that of vibrational spectra of imperfect crystals.

I. INTRODUCTION

WHEN a metal is in the crystalline state the motion of its conduction electrons is reasonably well understood in comparison with what is known about their behavior after the crystal melts. The main reason for this difference is that in the former case the single-particle energy eigenfunctions depend on the coordinates of all the ions only in a relatively simple manner due to the Bloch condition. Since the structure is periodic it is sufficient to solve the Schrödinger equation for only a single unit cell. The situation in a liquid metal is much more complicated. The single-particle energy eigenstates then depend on all the ionic coordinates in an intricate fashion, and all the static correlation functions that are necessary to describe the liquid state in complete detail will enter into the problem.

The difficulty caused by the lack of translational symmetry manifests itself right at the outset of a

calculation. In the crystalline state, the free-electron model with an effective mass serves as a reasonable starting point for perturbation theory in spite of the fact that the interaction between electrons and ions is not small. In the liquid state, the wave vector is not a good quantum number and hence the effective-mass approximation does not help. In principle, one is faced with infinite order perturbation theory right from the beginning. In fact it was an important advance, and gave much impetus to current work on electrons in liquid metals when Ziman¹ showed that one may start from free electrons and use perturbation theory provided the ions replaced by a suitably defined pseudo atoms whose interaction with the electrons is small and therefore can be treated in low-order perturbation theory.

A more fundamental approach to the problem has been provided by Edwards.^{2,3} He considered the dynamics of an electron moving in the potential field of N

* Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

† Permanent address: The University, Sheffield, United Kingdom.

¹ J. M. Ziman, *Phil. Mag.* **6**, 1013 (1961).

² S. F. Edwards, *Phil. Mag.* **3**, 1021 (1958).

³ S. F. Edwards, *Phil. Mag.* **6**, 617 (1961).

classical stationary scatters, and sought to solve for the Green's function $G^\pm(\mathbf{r}, \mathbf{r}'; \epsilon)$ satisfying the differential equation

$$[\frac{1}{2}\nabla^2 + \sum_n V(\mathbf{r} - \mathbf{R}_n) + \epsilon \pm i\eta]G^\pm(\mathbf{r}, \mathbf{r}'; \epsilon) = \delta(\mathbf{r} - \mathbf{r}'), \quad (1)$$

where \mathbf{r} is the position coordinate of the electron, ϵ is the energy variable, \mathbf{R}_n is the position of the n th scatterer, $V(\mathbf{r} - \mathbf{R}_n)$ is the interaction potential between the electron and the n th scatterer, and η is an infinitesimal constant. Clearly, $G^\pm(\mathbf{r}, \mathbf{r}'; \epsilon)$ depends on the position of all the scatterers. Since an experiment cannot distinguish between various configurations it is the ensemble averaged Green's function which is of interest. This may be defined as

$$\langle G^\pm(\mathbf{r}, \mathbf{r}'; \epsilon) \rangle = \int d\{\mathbf{R}_n\} f^N(\{\mathbf{R}_n\}) G^\pm(\mathbf{r}, \mathbf{r}'; \epsilon), \quad (2)$$

where $\{\mathbf{R}_n\}$ stands for a particular configuration specified by $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3 \dots \mathbf{R}_N$, $f^N(\{\mathbf{R}_n\})$ is the probability density that such configuration occurs, and $d\{\mathbf{R}_n\}$ is the infinitesimal volume element of the $3N$ -dimensional phase space spanned by the variables $\mathbf{R}_1, \mathbf{R}_2 \dots \mathbf{R}_N$. A more detailed discussion of the meaning of this averaging procedure was given by Kohn and Luttinger⁴ and also by Klauder.⁵ The simplest and most often sought of the information contained in the average Green's function is the density of states

$$n(\epsilon) = \frac{1}{\pi} \int d\mathbf{r}^3 \langle G(\mathbf{r}, \mathbf{r}; \epsilon) \rangle. \quad (3)$$

This model is a good starting point for most discussions of electrons in disordered systems. In particular, as was argued by Edwards,⁶ it is well suited to describe an electron moving in a liquid metal. Indeed, if the electron-electron interaction is neglected and it is assumed that the potential energy of an electron is a sum of contributions from each ion depending only on the separation between the electron and the ion, then the above model obtains. In that case the interaction potential $V(\mathbf{r} - \mathbf{R}_n)$ should be regarded as being the same as the interaction potential entering into a band-theory calculation for the same metal in the crystalline state. Having solved for the averaged Green's function $\langle G(\mathbf{r}, \mathbf{r}'; \epsilon) \rangle$ one only has to fill up the single-particle energy levels determined by the poles of $\langle G(\mathbf{r}, \mathbf{r}'; \epsilon) \rangle$ in accordance with the exclusion principle to obtain a realistic single-particle theory of the liquid metal.

Although there is no dearth of approximate solutions to this model problem⁷ no solution to date appears to be sufficiently accurate to justify extensive numerical cal-

culations of the density of states for realistic liquid-metal potentials. The difficulty lies in the requirement that a reasonable approximation must treat the potential to all orders in perturbation theory for it is certainly not small, it must not allow an electron to propagate freely between collisions for in a liquid the ionic potentials do overlap, and finally a reasonable approximation should account for some of the local order an electron sees.

It is the purpose of the present paper to present a calculational scheme which meets all three of these requirements. It treats the scattering of the electron from a single scatterer exactly, it allows for the fact that the electron is never free by introducing an averaged medium in which the electron travels between collisions and whose properties are determined in self-consistent manner, and finally a description of the short-range order is incorporated into the calculation through the radial distribution function.

The guiding spirit of the approach is the coherent-potential approximation first introduced, in the context of electrons in random alloys, by Soven⁸ and was applied subsequently to the vibrational properties of imperfect crystals by Taylor.⁹ It was also formulated for the case of electrons in liquid metals by Faulkner.¹⁰

This approximation views each scatterer as being immersed in a medium whose properties are determined by the requirement that the single-particle scattering due to the difference between the effective Hamiltonian H_{eff} which describes the medium and the exact Hamiltonian H would be zero on the average. Namely, one is to find a medium such that $\langle T_n \rangle = 0$, where T_n is the scattering operator for the n th scatterer. This condition completely defines $G^c(\mathbf{r}, \mathbf{r}'; \epsilon)$ the coherent-potential approximation to $\langle G(\mathbf{r}, \mathbf{r}'; \epsilon) \rangle$.

Recent successes of this method seem to warrant the conclusion that it is the first approximation to the model problem which does justice to its essential complexity. It fares well whether one compares its predictions with results of exact calculations for one-dimensional systems⁸ or one considers the general features of the approximate solutions. For example, it does not always split the band when applied to the problem of random alloy as does, incorrectly, the average t -matrix method of Korringa¹¹ and Beeby¹² at least in the form put forward by the latter author. It also satisfies a number of exact sum rules¹³ as was shown by Velický *et al.*¹⁴ Numerical results given by coherent-potential calculations for three-dimensional models of random alloys were compared extensively with other approxi-

⁸ P. Soven, Phys. Rev. **156**, 809 (1967).

⁹ D. W. Taylor, Phys. Rev. **156**, 1017 (1967).

¹⁰ J. S. Faulkner, Phys. Rev. (to be published).

¹¹ J. Korringa, J. Phys. Chem. Solids **1**, 252 (1958).

¹² J. L. Beeby, Proc. Phys. Soc. (London) **A279**, 82 (1964); Phys. Rev. **135**, A130 (1964).

¹³ S. F. Edwards, Proc. Phys. Soc. (London) **85**, 1 (1965).

¹⁴ B. Velický, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. **175**, 747 (1968).

⁴ W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

⁵ J. R. Klauder, Ann. Phys. (N. Y.) **14**, 43 (1961).

⁶ S. F. Edwards, Proc. Roy. Soc. (London) **267**, 518 (1962).

⁷ For an extensive review of electrons in disordered structures see N. F. Mott, Advan. Phys. **16**, 49 (1967).

mate solutions by Soven¹⁵ and Velický *et al.*¹⁴ and on all account they proved superior. This fact was further corroborated from a theoretical point of view by Faulkner¹⁰ who has shown that for the case of liquid metals the coherent-potential approximation is the same as the most sophisticated of a series of progressively more inclusive approximations derived by Klauder⁵ and independently by Matsubara and Toyozawa¹⁶ using an entirely different, diagrammatic technique. The power of the method is particularly well illustrated by the work of Onodera and Toyozawa¹⁷ who applied the approximate solution to the calculation of the conductivity of Frenkel excitons in mixed ionic crystals with considerable success.

It is also germane to the discussion that the very interesting calculation of the density of states for liquid iron by Anderson and McMillan¹⁸ bears a close resemblance to a coherent-potential calculation. While these authors do not follow in detail the prescription of that method, in order to improve upon the average t -matrix approximation they made use of the condition $\langle T_n \rangle = 0$ for determining an E -versus- \mathbf{k} dispersion relation. The ability of their treatment to deal with the effects of the d -band resonances on the density of states speaks well indeed for the power of the method.

However, in spite of its general plausibility the coherent-potential approximation has, in principle, a serious shortcoming; it takes no account of the correlation between the positions of the scatterers. The coherent-potential ansatz, which determines the Green's function $G^c(\mathbf{r}, \mathbf{r}'; \epsilon)$, is a condition on the scattering from a single, isolated scatterer immersed in the effective medium and hence it can take no account of any order in the distribution of the scatterers.

In the case of electrons in random alloys and phonons in imperfect crystals this might not matter much but for electrons in liquid metals the liquid structure is an essential feature of the problem. The new method to be introduced in Sec. V is a rather straightforward generalization of the coherent-potential approximation for the case where there is short-range order. What will be required for determining $G^c(\mathbf{r}, \mathbf{r}'; \epsilon)$ is that a group of ions whose positions are correlated should show no scattering due to the difference Hamiltonian $H - H_{\text{eff}}$ on the average.

In Sec. II a formulation of multiple scattering theory is given which explicitly takes into account all the correlations between the positions of the scatterers. In Sec. III the quasicrystalline approximation is introduced. This allows the description of the liquid to be given by only the radial distribution function. In Sec.

IV the coherent-potential approximation is reviewed for random distribution of scatterers. In Secs. V and VI the generalized coherent-potential approximation is given and discussed.

II. FORMULATION OF PROBLEM

Instead of the Green's function defined by Eq. (1) it is often more convenient to work with the propagator

$$G(z) = [z - p^2 - \sum_n V(\mathbf{r} - \mathbf{R}_n)]^{-1}, \quad (4)$$

where \mathbf{p} and \mathbf{r} are the electronic momentum and position operators, respectively, and z is an arbitrary complex number. This propagator is an operator whose matrix elements in the position representation give back the Green's function, i.e.,

$$G^\pm(\mathbf{r}, \mathbf{r}'; \epsilon) = \langle \mathbf{r} | G(\epsilon \pm i\eta) | \mathbf{r}' \rangle. \quad (5)$$

Note that the matrix elements are taken with respect to the eigenstates of the electron position operator, the coordinate of the scatterers being regarded as simple c -number random variables which define the interaction Hamiltonian. It is thus reasonable to assume, in order to be able to work with the propagator $G(z)$, that it makes no difference whether one averages the Green's function or the propagator with respect to these random variables. In other words the averaged propagator $\langle G(z) \rangle$ should still be a well-behaved operator in the Hilbert space spanned by the state vectors $|\mathbf{r}\rangle$ such that

$$\langle G^\pm(\mathbf{r}, \mathbf{r}'; \epsilon) \rangle = \langle \mathbf{r} | \langle G(\epsilon \pm i\eta) \rangle | \mathbf{r}' \rangle, \quad (6)$$

where the same prescription applies for averaging the propagator as was defined for the Green's function in Eq. (2). In what follows similar assumption will be made about all operators to which the averaging brackets $\langle \rangle$ are applied without further apology. A more rigorous discussion of the averaged Green's function and averaged propagators are given by Edwards¹⁹ in terms of density matrices.

It follows from Eq. (4) that the propagator $G(z)$ satisfies the operator equation

$$G(z) = G^0(z) + G^0(z) \sum_n V(\mathbf{r} - \mathbf{R}_n) G, \quad (7)$$

where

$$G^0(z) = 1/(z - p^2). \quad (8)$$

The usual approach to finding the Green's function $\langle G(\mathbf{r}, \mathbf{r}'; \epsilon) \rangle$ is to iterate Eq. (7) and thus generate a perturbation series in powers of the interaction potential $\sum_n V(\mathbf{r} - \mathbf{R}_n)$ for a particular configuration. One then averages this series term by term according to the prescription given by Eq. (2). Finally the matrix elements of the averaged propagator are taken as discussed above.

¹⁹ S. F. Edwards, *Advan. Phys.* **16**, 359 (1967).

¹⁵ P. Soven, *Phys. Rev.* **178**, 1136 (1969).

¹⁶ T. Matsubara and Y. Toyozawa, *Progr. Theoret. Phys. (Kyoto)* **26**, 739 (1961).

¹⁷ Y. Onodera and Y. Toyozawa, *J. Phys. Soc. Japan* **24**, 1341 (1968).

¹⁸ P. W. Anderson and W. L. McMillan, in *Proceedings of the International School of Physics, "Enrico Fermi" Course 37*, edited by W. Marshall (Academic Press Inc., New York, 1967).

In this paper an alternative approach provided by the multiple scattering theory of Lax²⁰ will be used. The advantage of this method over the straightforward perturbation expansion lies in the fact that in multiple scattering theory one separates the problem of an electron scattering from a single isolated scatterer from that of adding up the contributions to the total scattered wave due to all the scatterers. This property of the method, which was first exploited in connection with electrons in disordered systems by Korringa¹¹ lies at the very heart of the coherent-potential approximation in the discussion by Velický.¹⁴

Since one is dealing with the propagators, instead of the conventional formulation of the multiple scattering theory in terms of wave functions, it is best to follow the operator version of the theory as discussed by Velický *et al.*¹⁴ These authors defined a total scattering operator T by the relation

$$\sum_n V(\mathbf{r}-\mathbf{R}_n)G(z) = TG^0(z), \quad (9)$$

from which it follows that

$$G(z) = G^0(z) + G^0(z)TG^0(z). \quad (10)$$

They then showed that the fundamental equations of the multiple scattering theory which determine T may be written as

$$T = \sum_n Q_n, \quad (11)$$

$$Q_n = T_n + T_n \sum_{m \neq n} G^0 Q_m, \quad (12)$$

where the operators T_n , Q_n , and V_n are defined by the relations

$$T_n = V_n + V_n G^0 T_n, \quad (13)$$

$$Q_n = V_n + \sum_m V_m G^0 Q_n, \quad (14)$$

$$V_n = V(\mathbf{r}-\mathbf{R}_n). \quad (15)$$

To clarify the meaning of Eqs. (11) and (12) it is worthwhile to briefly make contact with the conventional formulation in terms of incoming and outgoing waves. Having this alternative formulation in mind will also help to discuss the relation between some of the results that will be obtained later and those derived previously by other authors. It follows from Eq. (10) that if an electron in the state $|\chi\rangle$ is incident upon the N scatterers the scattered wave is

$$|\psi^+\rangle = G^0 T |\chi\rangle. \quad (16)$$

On the other hand, the incoming wave to the n th scatterer is defined by the relation

$$T_n |\psi_n\rangle = Q_n |\chi\rangle. \quad (17)$$

Thus Eq. (11) is simply the assertion that the total outgoing wave is the sum of the outgoing waves from each scatterer. Furthermore, it follows from Eq. (12) that $|\psi_n\rangle = |\chi\rangle + \sum_{m \neq n} G^0 T_m |\psi_m\rangle$ which is just the statement that the incoming wave to the n th site is made up of two parts: the first being the incident wave in the absence of all the other scatterers, $|\chi\rangle$, and a second part which is produced by scattering at all the other sites of all the respective incoming waves, namely, $\sum_{m \neq n} G^0 T_m |\psi_m\rangle$.

Having thus obtained a prescription for determining the propagator $G(z)$ one must now seek the average $\langle G(z) \rangle$. Since $G^0(z)$ does not depend on the coordinates of the scatterers it follows from Eq. (10) that

$$\langle G(z) \rangle = G^0(z) + G^0(z) \langle T \rangle G^0(z). \quad (18)$$

Furthermore, upon averaging Eqs. (11) and (12) one obtains

$$\langle T \rangle = \sum_n \langle Q_n \rangle, \quad (19)$$

$$\langle Q_n \rangle = \langle T_n \rangle + \sum_{m \neq n} \langle T_n G^0 Q_m \rangle. \quad (20)$$

Clearly, these are not a set of closed equations like Eqs. (11) and (12). However, they may be turned into a set of closed equations by defining a set of partially averaged operators which will now be introduced.

At first, let us note that the scattering operator T_n which describes the scattering of the electron from the n th ion located at \mathbf{R}_n , in the absence of all the other ions depends only on \mathbf{R}_n out of the set $\{\mathbf{R}\}$. Hence, it will be written as $T_n = t(\mathbf{R}_n)$. The scattering operator Q_n which describes the scattering from the same ions but in the presence of other ions at $\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_{n-1}, \mathbf{R}_{n+1}, \dots, \mathbf{R}_N$ depends on the whole configuration $\{\mathbf{R}\}$. This dependence shall be made explicit by writing $Q_n = Q_n(\mathbf{R}_n; \{\mathbf{R}\}')$ where $\{\mathbf{R}\}'$ stands for all the position variables except \mathbf{R}_n . The partially averaged operators may now be defined as

$$\langle Q_n \rangle = \int d\{\mathbf{R}\} f^N(\{\mathbf{R}\}) Q_n(\mathbf{R}_n; \{\mathbf{R}\}'),$$

$$\langle Q_n(\mathbf{R}_n) \rangle = \int d\{\mathbf{R}\}' f^N(\mathbf{R}_n; \{\mathbf{R}\}') Q_n(\mathbf{R}_n; \{\mathbf{R}\}'), \quad (21)$$

$$\langle Q_n(\mathbf{R}_n; \mathbf{R}_m) \rangle = \int d\{\mathbf{R}\}'' f^N(\mathbf{R}_n, \mathbf{R}_m; \{\mathbf{R}\}'')$$

$$\times Q_n(\mathbf{R}_n; \{\mathbf{R}\}'),$$

$$\langle Q_n(\mathbf{R}_n; \mathbf{R}_m, \mathbf{R}_e) \rangle = \int d\{\mathbf{R}\}''' f^N(\mathbf{R}_n, \mathbf{R}_m, \mathbf{R}_e; \{\mathbf{R}\}''')$$

$$\times Q_n(\mathbf{R}_n; \{\mathbf{R}\}'),$$

where $f^N(\mathbf{R}_n, \{\mathbf{R}\}')$ is the conditional probability density

²⁰ M. Lax, Rev. Mod. Phys. **23**, 287 (1951).

that if it is known that the n th scatterer is at \mathbf{R}_n then the partial configuration $\{\mathbf{R}\}'$ obtains, $f^N(\mathbf{R}_n, \mathbf{R}_m; \{\mathbf{R}\}')$ and $f^N(\mathbf{R}_n, \mathbf{R}_m, \mathbf{R}_l; \{\mathbf{R}\}''')$ are the obvious generalizations of the conditional probability density $f^N(\mathbf{R}_n; \{\mathbf{R}\})$ for the cases where two and three ions position is assumed to be known in advance with $\{\mathbf{R}\}''$ standing for all the coordinates of the ions except two and $\{\mathbf{R}\}'''$ for all the coordinates except three. As to which two and three it should be clear from the context.

Equations satisfied by these partially averaged operators, $\langle Q_n(\mathbf{R}_n) \rangle$, $\langle Q_n(\mathbf{R}_n; \mathbf{R}_m) \rangle$, and so on, may be derived by performing the appropriate partial averages on Eq. (12). One thus obtains the following hierarchy of equations

$$\begin{aligned} \langle Q_n(\mathbf{R}_n) \rangle &= t(\mathbf{R}_n) + \sum_{m \neq n} \int d\mathbf{R}_m t(\mathbf{R}_n) \\ &\quad \times G^0 \langle Q_m(\mathbf{R}_m; \mathbf{R}_n) \rangle g^{(2)}(\mathbf{R}_n; \mathbf{R}_m), \quad (22) \\ \langle Q_n(\mathbf{R}_n; \mathbf{R}_m) \rangle &= t(\mathbf{R}_n) + \sum_{l \neq n} \int d\mathbf{R}_l t(\mathbf{R}_n) \\ &\quad \times G^0 \langle Q_l(\mathbf{R}_l; \mathbf{R}_m; \mathbf{R}_n) \rangle g^{(3)}(\mathbf{R}_n, \mathbf{R}_m; \mathbf{R}_l), \end{aligned}$$

where $g^{(2)}(\mathbf{R}_n; \mathbf{R}_m)$ is the conditional probability that if the n th ion is at \mathbf{R}_n then the m th ion is at \mathbf{R}_m , $g^{(3)}(\mathbf{R}_n, \mathbf{R}_m; \mathbf{R}_l)$ is the conditional probability that if the n th ion is at \mathbf{R}_n and the m th ion is at \mathbf{R}_m then the l th ion will be at \mathbf{R}_l .

For finite N , the hierarchy terminates and thus a closed set of equations are obtained, albeit it is a much larger set than the one represented by Eqs. (10) and (11). The conditional probabilities $g^{(2)}(\mathbf{R}_n; \mathbf{R}_m)$, $g^{(3)}(\mathbf{R}_n, \mathbf{R}_m; \mathbf{R}_l)$ are related to the static correlation functions which describe the liquid formed by the scatterers in thermal equilibrium. In the solid case such complete information is available, for the crystal structure can be determined by x-ray scattering. In fact, as shall be shown later, the above procedure reduces to the band-structure calculation of Korrington²¹ for an ordered lattice. However, for liquids, at the present, only the radial distribution function is known either experimentally or theoretically; hence, one must resort to approximations which decouple the hierarchy right after the first equation. In Sec. III a decoupling procedure will be considered which does just that.

III. QUASICRYSTALLINE APPROXIMATION

A simple but nontrivial decoupling of Eqs. (22) occurs if one sets

$$\langle Q_n(\mathbf{R}_n, \mathbf{R}_m) \rangle = \langle Q(\mathbf{R}_n) \rangle. \quad (23)$$

This is, in fact, the quasicrystalline approximation introduced by Lax²² for a wave multiple scattering in a

dense system. He used partially averaged wave functions instead of the partially averaged scattering operators employed in the present discussion. However, the connection is rather straightforward. It can be shown that his partially averaged wave functions may be obtained from the relations

$$\begin{aligned} T_n \psi^n(\mathbf{r}) &= \langle \mathbf{r} | \langle Q_n(\mathbf{R}_n) \rangle | \chi \rangle, \\ T_n \psi^{nm}(\mathbf{r}) &= \langle \mathbf{r} | \langle Q_n(\mathbf{R}_n, \mathbf{R}_m) \rangle | \chi \rangle, \end{aligned} \quad (24)$$

where $|\chi\rangle$ is a free particle state with appropriate boundary conditions and $\psi^n(\mathbf{r})$, $\psi^{nm}(\mathbf{r})$ are the electronic wave functions averaged over all but the n th, or n th and m th scatterer coordinates. In terms of these wave functions Lax²⁰ defined the quasicrystalline approximation as

$$\psi^n(\mathbf{r}) = \psi^{nm}(\mathbf{r}), \quad (25)$$

which is clearly equivalent to Eq. (23). The approximation is so-called because in the case of an ordered system the above relation is exact. Holding one scatterer fixed and averaging over all the others give the same result as holding two scatterers fixed while the averaging is performed when the probability distribution $f^N(\{\mathbf{R}\})$ is such that it is one for a particular configuration—the actual crystal structure—and zero for all the others. This is the basis of the claim that the present approach reduces to the band-structure calculation of Korrington²¹ for an ordered system.

Let us now return to the disordered system under discussion. If it is homogeneous then $g^{(2)}(\mathbf{R}_n; \mathbf{R}_m) = g^{(2)}(\mathbf{R}_n - \mathbf{R}_m)$ for any two ions, and in the quasicrystalline approximation the first member of the hierarchy in Eq. (22) takes the following form:

$$\begin{aligned} Q(\mathbf{R}) &= t(\mathbf{R}) + (N-1) \\ &\quad \times \int d^3\mathbf{R}' t(\mathbf{R}) G^0 Q(\mathbf{R}') g(\mathbf{R} - \mathbf{R}'), \quad (26) \end{aligned}$$

where the suffixes on Q_n and \mathbf{R}_n have been neglected for in this approximation all the functions $\langle Q_n(\mathbf{R}) \rangle$ are the same, $Q(\mathbf{R})$, and $g(\mathbf{R})$ is just the radial distribution function (it is normalized to unity) available from x-ray diffraction or neutron scattering experiments.

To ascertain the level of approximation achieved by Eq. (26) consider the case of randomly distributed scatterers. Then if the extension of the ions is neglected

$$g(\mathbf{R}) = 1/\Omega$$

and Eq. (26) reduces to

$$Q(\mathbf{R}) = t(\mathbf{R}) [1 + (N-1)G^0 \langle Q \rangle], \quad (27)$$

where

$$\langle Q \rangle = \frac{1}{\Omega} \int d\mathbf{R} Q(\mathbf{R}).$$

²¹ J. Korrington, *Physica* **13**, 392 (1947).

²² M. Lax, *Phys. Rev.* **85**, 621 (1952).

By integrating both sides of Eq. (27) one obtains

$$\langle Q \rangle = \langle t \rangle [1 + (N-1)\langle Q \rangle], \quad (28)$$

which is the single site approximation for a homogeneous system discussed by Velický *et al.*¹⁴ Thus the quasicrystalline approximation nicely interpolates between complete order, where it is exact, and complete disorder where it is the same as the single site approximation.

The solution of Eq. (28) is

$$\langle Q \rangle = \frac{\langle t \rangle}{1 - NG^0 \langle t \rangle}, \quad (29)$$

where

$$\langle t \rangle = \frac{1}{\Omega} \int d\mathbf{R} t(\mathbf{R}), \quad (30)$$

and the 1 in $N-1$ had been neglected.

Since $\langle T \rangle = N \langle Q \rangle$ the averaged propagator, given in Eq. (18), is of the form

$$\langle G \rangle = G^0 \left[1 + N \frac{\langle t \rangle G^0}{1 - NG^0 \langle t \rangle} \right] = \frac{G^0}{1 - NG^0 \langle t \rangle}. \quad (31)$$

Note that the operator $\langle t \rangle$ is diagonal in the momentum representation, for it follows from Eq. (13) that

$$\langle \mathbf{p} | t(\mathbf{R}) | \mathbf{p}' \rangle = t_{\mathbf{p}\mathbf{p}'} e^{-i(\mathbf{p}-\mathbf{p}') \cdot \mathbf{R}}, \quad (32)$$

where $t_{\mathbf{p}\mathbf{p}'}$, the usual scattering matrix, is given by the integral equation

$$t_{\mathbf{p}\mathbf{p}'} = V_{\mathbf{p}\mathbf{p}'} + \sum_{\mathbf{p}''} V_{\mathbf{p}\mathbf{p}''} G_{\mathbf{p}''}^0 t_{\mathbf{p}''\mathbf{p}'}, \quad (33)$$

with $\langle \mathbf{p} | V(\mathbf{r}) | \mathbf{p}' \rangle = V_{\mathbf{p}\mathbf{p}'}$ and $G_{\mathbf{p}''}^0 = \langle \mathbf{p}'' | G^0 | \mathbf{p}'' \rangle$, and therefore

$$\langle \mathbf{p} | \langle t \rangle | \mathbf{p}' \rangle = t_{\mathbf{p}\mathbf{p}'} \delta(\mathbf{p} - \mathbf{p}'). \quad (34)$$

Hence, in the momentum representation

$$\langle G(\mathbf{p}, z) \rangle = \langle \mathbf{p} | G(z) | \mathbf{p} \rangle = 1/(z - p^2 - N t_{\mathbf{p}\mathbf{p}}), \quad (35)$$

where $t_{\mathbf{p}\mathbf{p}}$ is the forward scattering amplitude.

The form for $\langle G(\mathbf{p}, z) \rangle$ may now be recognized as the average t -matrix approximation first given by Korrington¹¹ and later used by Beeby¹² for random alloys. In Lax's treatment the same result is obtained and since he was concerned with a scatter wave traveling in a dense liquid he regarded the forward scattering amplitude as the index of refraction describing the macroscopic "dielectric" properties of the medium.

One may, therefore, conclude that Eq. (26) is the generalization of the averaged t -matrix approximation for the case where there is short range order. As such, it probably suffers from the same inadequacies. That is to say, the shortcomings of the averaged t -matrix approximation, as they are described in the work of Soven¹⁵ and Velický *et al.*,¹⁴ would show up in full force if the numerical consequences of Eq. (26) were explored

in detail. Nevertheless it seems worthwhile to explore the implications of Eq. (26) a bit further for they shall be useful as a basis of comparison when the generalized coherent-potential approximation will be introduced in Sec. V.

By taking the matrix elements of Eq. (26) in the momentum representation one obtains

$$Q_{\mathbf{p}\mathbf{p}'}(\mathbf{R}) = t_{\mathbf{p}\mathbf{p}'} e^{-i(\mathbf{p}-\mathbf{p}') \cdot \mathbf{R}} + (N-1) \sum_{\mathbf{p}''} \int d^3\mathbf{R}' t_{\mathbf{p}\mathbf{p}''} e^{-i(\mathbf{p}-\mathbf{p}'') \cdot \mathbf{R}} G_{\mathbf{p}''}^0 Q_{\mathbf{p}''\mathbf{p}'}(\mathbf{R}), \quad (36)$$

where

$$\langle \mathbf{p} | Q(\mathbf{R}) | \mathbf{p}' \rangle = Q_{\mathbf{p}\mathbf{p}'}(\mathbf{R}).$$

If one iterates Eq. (36) and examines the \mathbf{R} dependence of each term one can easily see that the solution of Eq. (36) will be of the form

$$Q_{\mathbf{p}\mathbf{p}'}(\mathbf{R}) = Q_{\mathbf{p}\mathbf{p}'} e^{-i(\mathbf{p}-\mathbf{p}') \cdot \mathbf{R}}, \quad (37)$$

where

$$Q_{\mathbf{p}\mathbf{p}'} = t_{\mathbf{p}\mathbf{p}'} + \sum_{\mathbf{p}''} t_{\mathbf{p}\mathbf{p}''} G_{\mathbf{p}''}^0 Q_{\mathbf{p}''\mathbf{p}'} g(\mathbf{p}'' - \mathbf{p}'), \quad (38)$$

with

$$g(\mathbf{p}'' - \mathbf{p}) = \int d\mathbf{R} e^{-i(\mathbf{p}-\mathbf{p}'') \cdot \mathbf{R}} g(\mathbf{R}). \quad (39)$$

Clearly the average Q operator $\langle Q \rangle$ is diagonal in the momentum representation since

$$\langle \mathbf{p} | \langle Q \rangle | \mathbf{p}' \rangle = \Omega^{-1} \int d\mathbf{R} \langle \mathbf{p} | Q(\mathbf{R}) | \mathbf{p}' \rangle = Q_{\mathbf{p}\mathbf{p}} \delta(\mathbf{p} - \mathbf{p}'). \quad (40)$$

Thus the averaged Green's function will also be diagonal, taking the form

$$\langle G(\mathbf{p}, z) \rangle = G_{\mathbf{p}}^0 + G_{\mathbf{p}}^0 Q_{\mathbf{p}\mathbf{p}} G_{\mathbf{p}}^0. \quad (41)$$

This should come as no surprise since the presence of the short-range order does not destroy the homogeneity of the system.

In summary, to calculate the Green's function in the quasicrystalline approximation discussed in this section, one must solve Eq. (13) for the single-particle scattering matrix $t_{\mathbf{p}\mathbf{p}'}$ in terms of a given potential $V_{\mathbf{p}\mathbf{p}'}$; then taking the radial distribution function from experiments, or from a Percus-Yevick hard-spheres calculation one must proceed to solve Eq. (38) for $Q_{\mathbf{p}\mathbf{p}'}$. Finally $\langle G(\mathbf{p}, z) \rangle$ is obtained by substituting $Q_{\mathbf{p}\mathbf{p}}$ into Eq. (41).

A theory equivalent to the above calculation has been worked out by Ziman²³ in considerably more detail for a specific example of muffin-tin potentials; therefore, we shall not develop it any further.

In concluding this section it should be noted that the quasicrystalline approximation discussed in this section

²³ J. M. Ziman, Proc. Phys. Soc. (London) **88**, 387 (1966).

is an alternative way of treating short-range order to the geometric approximation used by Edwards⁶ and Beeby.¹² It appears to be a better approximation for if one treats the scattering matrix $t_{pp'}$ in the Born approximation, i.e., one replaces it by $V_{pp'}$ and then iterates Eq. (38) Edwards result obtains provided terms which contain odd powers of $V_{pp'}$ are neglected and in the even terms every other $g(\mathbf{p}-\mathbf{p}')$ is set equal to $\delta(\mathbf{p}-\mathbf{p}')$. It seems that by picking out the coherent part of the scattered waves and treating them more correctly than the incoherent parts, multiple scattering theory allows an approximation which requires only the crude knowledge of liquid correlations afforded by the radial distribution function. This, of course, is of considerable importance for at the present state of the theory of liquid correlations any simplifying assumption about these correlations is likely to be hazardous.

IV. COHERENT-POTENTIAL APPROXIMATION IN ABSENCE OF SHORT-RANGE ORDER

As mentioned in the Introduction, the average t -matrix approximation fails because it is the free particle Green's function which is used to calculate the scattering matrix t_{pp} . The scattering is assumed to take place as in free space. This is clearly inconsistent with the end result that the electron is not free but described by a dressed propagator, Eq. (35). The coherent-potential approximation removes this inconsistency and thereby improves the approximation considerably. However, as will be shown, this approximation scheme only works for the case of randomly distributed scatterers. It will be the object of the next section to introduce a generalization of the method capable of treating correlated scatterers. In order to facilitate the discussion of this generalized procedure, the form the coherent-potential approximation takes when applied to electrons in liquid metals will now be outlined briefly, following the treatment of Faulkner.¹⁰

The method is based on the philosophy that a simple medium can be found such that when an electron is immersed in that medium it will behave as if it were moving in the potential field $V(\mathbf{r}-\mathbf{R}_n)$. On the average, the medium is described by the coherent potential w_p which is constant in space but possibly dependent on momentum operator \mathbf{p} . Since it is designed to simulate $V(\mathbf{r}-\mathbf{R}_n)$ only on the average, it does not depend on the positions of the scatterers; hence, the adjective "simple."

One may remark in passing that similar philosophy is often used in statistical mechanics when interaction with a random system, like a thermal reservoir, is described by a velocity-dependent frictional force.

The Green's function which describes the motion of an electron in this medium satisfies the equation

$$\left(z - p - \frac{N}{\Omega} w_p\right) G^e(\mathbf{p}, z) = 1, \quad (42)$$

whose solution is simply

$$G^e(\mathbf{p}, z) = \frac{1}{z - p^2 - (N/\Omega) w_p}. \quad (43)$$

The question is, then, how to choose the coherent potential w_p in order that $G^e(\mathbf{p}, z)$ would best describe the average motion of an electron in the potential field $\sum_n V(\mathbf{r}-\mathbf{R}_n)$.

To answer this question, write the Hamiltonian for the electron in the form

$$H = p^2 + \frac{N}{\Omega} w_p + \sum_n \left[V(\mathbf{r}-\mathbf{R}_n) - \frac{1}{\Omega} w_p \right], \quad (44)$$

where $(1/\Omega)w_p$ is the coherent potential per scatterer, and consider the problem of an electron moving in the medium according to the propagator G^e and scatters from the effective ionic potentials $\tilde{V}(\mathbf{R}_n) = V(\mathbf{r}-\mathbf{R}_n) - (1/\Omega)w_p$. The scattering from an isolated effective ion located at \mathbf{R} is described by the scattering matrix that satisfies the integral equation

$$\tilde{l}(\mathbf{R}) = \tilde{V}(\mathbf{R}) + \tilde{V}(\mathbf{R}) G^e \tilde{l}(\mathbf{R}). \quad (45)$$

One may now determine G^e or, alternatively, $(1/\Omega)w_p$, from the requirement that

$$\langle \tilde{l} \rangle = \int d^3R \tilde{l}(\mathbf{R}) = 0. \quad (46)$$

That is to say, the medium is so chosen that on the average there is no scattering from the difference potential $V(\mathbf{r}-\mathbf{R}) - (1/\Omega)w_p$. This is the Coherent Potential prescription first proposed by Soven.⁸ Faulkner¹⁰ has shown that in the limit where $N \rightarrow \infty$, $\Omega \rightarrow \infty$ such that $N/\Omega = \rho$, Eq. (46) implies that

$$w_p = \hat{t}_{pp},$$

where

$$\hat{t}_{p,p'} = V_{p,p'} + \sum_{p''} V_{p,p''} G_{p'',p'}^e \hat{t}_{p'',p'}, \quad (47)$$

with

$$\langle G \rangle = G^e.$$

Clearly, the inconsistency mentioned at the beginning of this section is removed. The scattering matrix which enters as the self-energy into the determination of $\langle G \rangle$ is calculated using the same dressed propagator as the one it determines. The same self-consistent internal propagator modification was obtained in a different way by Klauder⁵ and Matsubara and Toyozawa.¹⁶

It will be useful to look at the problem from a slightly different point of view afforded by the multiple scattering theory discussed in the previous section. To begin with, note that the Hamiltonian given by Eq. (44) is exact. If the problem of an electron moving in the

medium and scattering from the effective ions could be solved exactly, the solution would not depend on w_p . If, however, one solves this problem in the quasicrystalline approximation with no short-range order according to the discussion in Sec. III, the result will depend on w_p and may be summarized as follows:

$$\langle G \rangle = G^e + G^e \langle \tilde{T} \rangle G^e, \quad (48)$$

$$\langle \tilde{T} \rangle = N \langle \tilde{Q} \rangle = \langle \tilde{t} \rangle / (1 - N G^e \langle \tilde{t} \rangle), \quad (49)$$

$$\langle G(\mathbf{p}, z) \rangle = \frac{1}{z - p^2 - (1/\Omega)w_p - \tilde{t}_{pp}(w_p)}, \quad (50)$$

where the operators \tilde{Q} , \tilde{T} are the obvious generalizations of Q and T for the effective scatterers just as $\tilde{t}(\mathbf{R})$, given by Eq. (45), is the generalization of the operator $t(\mathbf{R})$ given in Eq. (33).

Clearly, the approximate solution given above depends on $(1/\Omega)w_p$; that is to say, depends on the zeroth-order approximation one starts from. Treated as an adjustable parameter $(1/\Omega)w_p$ may now be used to improve on the average t -matrix approximation by taking the most favorable zeroth-order approximation. The coherent-potential prescription which requires that $\langle \tilde{t} \rangle = 0$ or $\tilde{t}_{pp}(w_p) = 0$ can thus be seen as a prescription for making the average t -matrix approximation consistent, for $\langle \tilde{t} \rangle = 0$ implies that $\langle G \rangle = G^e$.

Keeping this interpretation in mind, one may now turn to the question whether a coherent potential may not be found, even for the case when there is short-range order, for, as will now be shown in that case the above procedure does not work.

V. GENERALIZED COHERENT-POTENTIAL APPROXIMATION

As was argued in Sec. III, the quasicrystalline approximation is the natural generalization of the averaged t -matrix approximation to the case where there is short-range order. In Sec. IV, it was shown that the coherent-potential approximation is a way of correcting the averaged t -matrix approximation by making it consistent. It is thus clear that one should seek the generalization of the coherent-potential approximation to the case where there is short-range order by making the quasicrystalline approximation consistent in the same sense.

Following the procedure of the previous section with the difference that now short-range order is allowed to play a role, one may again consider the electron moving in the medium, characterized by w_p , and scattering from the potentials $\tilde{V}_n = V(\mathbf{r} - \mathbf{R}_n) - (1/\Omega)w_p$. Then, in the quasicrystalline approximation,

$$\langle G \rangle = G^e + N G^e \langle \tilde{Q} \rangle G^e, \quad (51)$$

where

$$\langle \tilde{Q} \rangle = \int d\mathbf{R} \tilde{Q}(\mathbf{R})$$

and $\tilde{Q}(\mathbf{R})$ is the solution of the equation

$$\tilde{Q}(\mathbf{R}) = \tilde{t}(\mathbf{R}) + (N-1) \int d^3\mathbf{R}' \tilde{t}(\mathbf{R}) G^e \tilde{Q}(\mathbf{R}') g(\mathbf{R} - \mathbf{R}'), \quad (52)$$

with $\tilde{t}(\mathbf{R})$ given by Eq. (45).

These are then the fundamental equations of the new approach. The problem is how to choose the coherent potential w_p which adequately represents the influence exerted by a set of correlated scatterers on an electron.

Unfortunately, Eq. (52) in its present form cannot be solved as conveniently as for a random system where $g(\mathbf{R}) = 1/\Omega$. However, it is clear from Eq. (52) that $\langle \tilde{t} \rangle = 0$ no longer implies $\langle \tilde{Q} \rangle = 0$ and, therefore, G^e obtained from the coherent-potential condition that $\langle \tilde{t} \rangle = 0$ is no longer the same as the averaged propagator $\langle G(\mathbf{p}, z) \rangle$, which is given by Eq. (51). Thus, though a dressed propagator G^e is used to calculate $\langle \tilde{t} \rangle$ and $\langle G \rangle$, it is not the same as the averaged propagator $\langle G \rangle$, and one is back to the same sort of inconsistency as in the case of the averaged t -matrix approximation.

In a way this inconsistency should not be surprising. The condition from which the coherent potential is determined, namely, that $\langle \tilde{t} \rangle = 0$, does not involve any information about the distribution of the scatterers. Hence, the medium cannot be expected to represent consistently the averaged behavior of an electron which moves among scatterers whose positions are correlated.

The point of this paper is to suggest that the more general condition

$$\langle \tilde{Q} \rangle = 0 \quad (53)$$

be used to determine the medium instead of the conventional coherent-potential prescription that $\langle \tilde{t} \rangle = 0$.

In other words, the generalized coherent potential should be determined by the requirement that the total scattered wave from an effective ion at \mathbf{R} , that is the scattered wave which is calculated without neglecting the presence of the other ions, should be zero on the average instead of the scattered wave from an isolated effective ion.

Obviously, the generalized coherent-potential prescription given by Eq. (53) ensures consistency for it immediately follows from Eq. (51) that $\langle G \rangle = G^e$ where G^e or $(1/\Omega)w_p$ is now obtained by solving Eq. (53).

It is also clear that the coherent potential now depends on the degree of short-range order present for $\tilde{Q}(\mathbf{R})$ being the partially averaged operator which gives the scattered wave from an effective ion at \mathbf{R} in the presence of all the ions, unlike $\tilde{t}(\mathbf{R})$, depends on the radial distribution function $g(\mathbf{R})$.

It is reassuring to note that in the limit of randomly distributed scatterers the new condition is equivalent to the coherent-potential condition for, as can be seen from Eq. (49), in this limit $\langle \tilde{Q} \rangle = 0$ implies $\langle \tilde{t} \rangle = 0$.

In order to explore the consequences of Eq. (53), note that the solution to Eq. (45) may be written as

$$\tilde{t}(\mathbf{R}) = \tilde{V}(\mathbf{R}) / [1 - G^e \tilde{V}(\mathbf{R})]. \quad (54)$$

By substituting this expression into Eq. (52), and then rearranging terms, one obtains the following equation for $\tilde{Q}(\mathbf{R})$:

$$\tilde{Q}(\mathbf{R}) = \tilde{V}(\mathbf{R}) + \int d^3\mathbf{R}' \tilde{V}(\mathbf{R}) G^e Q(\mathbf{R}') g(\mathbf{R} - \mathbf{R}'), \quad (55)$$

where

$$g(\mathbf{R} - \mathbf{R}') = \delta(\mathbf{R} - \mathbf{R}') + (N-1) \mathcal{G}(\mathbf{R} - \mathbf{R}'),$$

which is just the van Hove correlation function $\mathcal{G}(\mathbf{r}, t)$ evaluated at $t=0$.

It is rather tedious but straightforward algebra to show that the solution of Eq. (55) may be written as

$$\begin{aligned} \tilde{Q}_{\mathbf{p}, \mathbf{p}'}(\mathbf{R}) = & \frac{1}{1 + (1/\Omega) w_{\mathbf{p}} G_{\mathbf{p}}^e \mathcal{G}(\mathbf{p} - \mathbf{p}')} \\ & \times \tilde{Q}_{\mathbf{p}, \mathbf{p}'} \frac{1}{1 + (1/\Omega) w_{\mathbf{p}'} G_{\mathbf{p}'}^e S_0} e^{-i(\mathbf{p} - \mathbf{p}') \cdot \mathbf{R}} \\ & - \frac{(1/\Omega) w_{\mathbf{p}}}{1 + (1/\Omega) w_{\mathbf{p}} G_{\mathbf{p}}^e S_0} \delta_{\mathbf{p} \mathbf{p}'}, \end{aligned} \quad (56)$$

where

$$\tilde{Q}_{\mathbf{p}, \mathbf{p}'} = V_{\mathbf{p}, \mathbf{p}'} + \sum_{\mathbf{p}''} V_{\mathbf{p} \mathbf{p}''} G_{\mathbf{p}''}^e \tilde{Q}_{\mathbf{p}'', \mathbf{p}'} \hat{g}(\mathbf{p}'' - \mathbf{p}'), \quad (57)$$

with

$$\hat{g}(\mathbf{p}'' - \mathbf{p}') = \frac{\mathcal{G}(\mathbf{p}'' - \mathbf{p}')}{1 + (1/\Omega) w_{\mathbf{p}'} G_{\mathbf{p}'}^e \mathcal{G}(\mathbf{p}'' - \mathbf{p}')} \quad (58)$$

and

$$S_0 = \int d\mathbf{R} \mathcal{G}(\mathbf{R}). \quad (59)$$

One may now apply the generalized coherent-potential prescription given by Eq. (53) to the expression for $\tilde{Q}_{\mathbf{p}, \mathbf{p}'}(\mathbf{R})$ given in Eq. (56). It then follows that

$$w_{\mathbf{p}} = \tilde{Q}_{\mathbf{p} \mathbf{p}} \quad (60)$$

in the limit where $N \rightarrow \infty$ and $\Omega \rightarrow 0$ but $N/\Omega = \rho$ is a finite density.

Clearly, Eqs. (57) and (60) together with the definition of G^e completely define the generalized coherent-potential approximation for the case where there is short-range order. As such it is the generalization of Eq. (47). Indeed, in the limit of complete disorder described by $\mathcal{G}(\mathbf{R}) = \delta(\mathbf{R} - \mathbf{R}') + (N-1)/\Omega$ it follows from Eq. (57) that $\tilde{Q} = \hat{I}$.

Thus, the calculational procedure suggested by the generalized coherent-potential prescription is that given a potential $V_{\mathbf{p} \mathbf{p}'}$ and a radial distribution function $g(\mathbf{R})$, one must solve Eqs. (57) and (60) self-consistently and then the average Green's function is given by G^e .

Unfortunately, it does not seem possible to find an analytic solution to Eqs. (57) and (60). Even for the simplest model of δ -function interaction potentials, $w_{\mathbf{p}}$ turns out to depend on \mathbf{p} in contradistinction to the case of random distribution of scatterers treated by Yonezawa²⁴ where one is able to solve for $w_{\mathbf{p}}$ by virtue of the fact that it turns out not to depend on \mathbf{p} .

However, it is hoped that numerical solutions for a one-dimensional system and for realistic three-dimensional potentials will be given in future publications.

VI. DISCUSSION

The main result of this paper is the new approximation to the averaged Green's function, for an electron moving in the potential field of N stationary scatterers, given by the simultaneous solution of Eqs. (57), (60), and (42). As was shown in the previous section, this approximation was obtained from a generalized coherent-potential ansatz given by Eq. (53). Because of the fact that in the present method it is the scattering operator $Q(\mathbf{R})$, which describes the scattering from an ion at \mathbf{R} in the presence of all the other ions, is required to vanish on the average, this approximation, in contrast to that obtained from the conventional coherent-potential prescription given by Eq. (46), takes into account the presence of short-range order. Because an appeal to the quasicrystalline approximation had to be made in calculating $Q(\mathbf{R})$ the short-range order enters into the determination of the averaged Green's function only through the radial distribution function.

In the limit of crystalline order the procedure is exact, for in this case the radial distribution function

$$g(\mathbf{R}) = \langle \sum_{n \neq m} \delta(\mathbf{R} - \mathbf{R}_n + \mathbf{R}_m) \rangle = \sum_{n \neq m} \delta(\mathbf{R} - \mathbf{R}_n + \mathbf{R}_m) \quad (61)$$

contains all information about the distribution of scatterers. To see what happens in this limit recall that for crystalline order the quasicrystalline approximation is exact, hence the equation for $Q(\mathbf{R})$ is exact, therefore, by solving Eq. (26) one is solving the problem exactly. In that case, as was pointed out in Sec. III, the coherent potential $w_{\mathbf{p}}$ drops out of the problem. In fact, the procedure reduces to the band-theory calculation of Korringa,²¹ and Kohn and Rostoker.²⁵ To be quite explicit let us substitute Eq. (61) into Eq. (26) and write

$$Q(\mathbf{R}_n) = \hat{I}(\mathbf{R}_n) + \sum_{m \neq n} [\hat{I}(\mathbf{R}_n) G^0 Q(\mathbf{R}_m)].$$

It then follows that in the wave-function representation sketched in Sec. II,

$$|\psi^+\rangle = |\chi\rangle + G_0 \sum_n T_n |\psi_n^+\rangle, \quad (62)$$

$$|\psi_n^+\rangle = |\chi\rangle + G_0 \sum_{m \neq n} T_m |\psi_m^+\rangle, \quad (63)$$

²⁴ F. Yonezawa, Progr. Theoret. Phys. (Kyoto) **31** (1964).

²⁵ W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

which is the usual starting point for the Korringa-Kohn-Rostoker (KKR) method.

In view of the fact that in this limit the coherent potential w_p drops out of the problem the above result should not be surprising, for without w_p the present method is the same as the average t -matrix method which, as was argued by Beeby,¹² reduces to the KKR calculation.

In the opposite limit of randomly distributed scatterers, as was shown in Sec. V, the present method is the same as the conventional coherent-potential procedure. Thus, the present method is seen to be capable of treating, in a unified manner, problems involving all degrees of order. It is, however, not yet clear how well it works for intermediate cases. This question will have to be decided when numerical results become available and will no doubt depend on the ratio of coherence length ξ to the inverse of the spatial damping coefficient, $\text{Im}Z(\epsilon)$, where $z(\epsilon) = \mathbf{p}(\epsilon) + i\Gamma(\epsilon)$ is the solution of the equation

$$\epsilon - z^2 - t_{zz}(\epsilon) = 0. \quad (64)$$

It must, however, be stressed that the approximation treated in this paper is not an expansion either in powers of $\xi\Gamma(\epsilon)$ or $1/\xi\Gamma(\epsilon)$ and appears to be applicable to the full range of cases discussed by Edwards.⁶

Although the generalized coherent-potential method has been presented in terms appropriate for discussing electrons in liquid metals, it is clearly applicable to other problems where the conventional coherent-potential method had been found useful and it is desirable to have a theory which takes into account correlations between

scattering centers. A case in point is that of electrons in random substitutional alloys. Though genuine correlations do play a part in certain x-ray scattering experiments,²⁶ in this case, past efforts have mainly concentrated on obtaining an approximation which treats correlation among impurity sites only to the extent that the possibility of two impurities occupying the same site is excluded. Both of these type of correlations have been treated recently by Ayier, Elliott, Krumhansl, and Leath.²⁷ It is hoped that the present method will be applied to this problem in a future publication in order to facilitate a comparison.

Similar remarks apply to the problem of thermal vibrations in imperfect crystals^{9,28} where a method for compensating against multiple occupancy of sites by defects have recently been proposed by Leath.²⁹

ACKNOWLEDGMENTS

I would like to thank Dr. J. S. Faulkner for introducing me to the coherent-potential method and for many helpful discussions in connection with the present work. I would also like to express my appreciation of the hospitality extended to me by the Metals and Ceramics Division of the Oak Ridge National Laboratory where most of the work was performed.

²⁶ B. E. Warren, *X-Ray Diffraction* (Addison-Wesley Publishing Co., Reading, Mass., 1969).

²⁷ R. N. Ayier, R. J. Elliott, J. A. Krumhansl, and P. L. Leath, *Phys. Rev.* **181**, 1006 (1969).

²⁸ R. W. Davies and J. S. Langer, *Phys. Rev.* **131**, 163 (1963).

²⁹ P. L. Leath, *Phys. Rev.* **171**, 725 (1968).