Simplified derivation of the matrix coherent-potential approximation for off-diagonal random alloys*

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A simple matrix generalization of the effective-medium approach to the coherent-potential approximation (CPA) permits the inclusion of off-diagonal disorder in a straighforward fashion. This derivation has the advantages of simplicity and ease of generalization to the n-site CPA. Results are obtained for electrons and for phonons in a disordered binary alloy. The electronic derivation reduces to the solution obtained by Blackman *et al.* while phonon results are new.

I. INTRODUCTION

The simple one-band tight-binding model with diagonal disorder[1] has been popular in treatments of the theory of disordered systems. Inclusion of off-diagonal randomness adds a limited amount of realism to this model. Various generalizations of the coherent-potential approximation (CPA) exist for this model,[2] with certain restrictions on the model parameters. These generalizations are all special cases of the theory developed by Blackman *et al.*[3] (to be referred to as the BEB theory). However, the latter theory was derived by a relatively complicated diagrammatic summation and, further, only considered electronic systems. In contrast to the diagrammatic approach, the effective-medium derivation of the CPA is attractive because (i) it is simple, (ii) it aids physical insight into the approximations employed, and (iii) it can be easily generalized to the n-site CPA (CPn). Hence, an effective-medium approach to off-diagonal CPA would have some value, particularly in that it would permit any advances in the technology for CPn to be generalized to include off-diagonal disorder. Such a generalization will be presented for electrons (Sec. II) and for phonons (Sec. III). The derivation includes some detail. However, in essence the theory is an exact parallel of the development for diagonal randomness[4] and as such, is quite straightforward. The essential difference is the replacement of the Green's function (and associated quantities) by matrices. The final solutions are to be found in Eqs. (22)–(25) for electrons and Eqs. (38)–(42) for phonons. The crucial step is the factoring of the matrix T matrix which occurs in Eq. (17).

This approach clarifies a brief observation made in a letter by Blackman[5] that the BEB solution, when cast in matrix form, acquires a very simple structure. Kerker[6] has suggested a short derivation of this matrix result. However, while the (correct) final result may be obtained by a matrix generalization of a suitable self-consistency condition [his Eq. (7)], the derivation leading up to this equation [his Eqs. (2)–(6)] cannot all be directly generalized to matrix form. Specifically, the 2×2 mass operator matrix has nonzero, off-diagonal components. However, a defining equation for his mass operator [his Eq. (5)] in matrix form only admits diagonal components, since the matrix generalization of the quanities on the right-hand side of this equation, as defined in his Eq. (8), are diagonal.[7] The final matrix solution remains an ansatz. In addition, generalizations of Kerker's procedure to CPn are not transparent.

II. MATRIX T MATRIX FOR ELECTRONS

We will follow the model and notation introduced in BEB. After defining our Hamiltonian, Green's function, etc., we will proceed to find an exact solution to this disordered A_xB_{1-x} binary-alloy problem in terms of a matrix T matrix. If we decouple this T matrix, factoring out a single-site T matrix exactly as is done in the scalar case,[4] and then set the average of the single-site matrix T matrix to zero, we obtain the CPA self-consistency condition for off-diagonal disorder. Generalizations to CPn follow immediately by paralleling the scalar theory. The derivation will have a minimum of accompanying verbiage, since the steps mimic the derivation for the scalar case.[4]

The model Hamiltonian is

$$H=\sum_i \epsilon_i c_i^\dagger c_i+\sum_{ij} W_{ij}\, c_i^\dagger c_j\,, \tag{1}$$

where the site energies $\epsilon_i(=\epsilon_A, \epsilon_B)$ and transfer integrals $W_{ij}(=W_{ij}^{AA}$, etc.) are both configuration dependent. We define the matrix Green's function, locator and transfer integral, respectively, as

$$\underline{G}_{ij}\equiv\begin{bmatrix} x_i x_j G_{ij} & x_i y_j G_{ij} \\ y_i x_j G_{ij} & y_i y_j G_{ij}\end{bmatrix}\,, \tag{2}$$

$$\underline{g}(\omega)\equiv\begin{bmatrix} \dfrac{x_i}{\omega-\epsilon_A} & 0 \\ 0 & \dfrac{y_i}{\omega-\epsilon_B}\end{bmatrix}\,, \tag{3}$$

$$\underline{W}_{ij} \equiv \begin{bmatrix} W_{ij}^{AA} & W_{ij}^{AB} \\ W_{ij}^{BA} & W_{ij}^{BB} \end{bmatrix}, \tag{4}$$

where we introduce the projection operator $x_i = 1 - y_i$, which is unity if i is on A site, and zero other otherwise.

The equation of motion for $\underline{G}$ is[6]

$$\underline{G}_{ij}(\omega) = \underline{g}_i(\omega)\delta_{ij} + \underline{g}_i\underline{W}_{ij}\underline{g}_j + \underline{g}_i\underline{W}_{il}\underline{g}_l\underline{W}_{lj}\underline{g}_j + \cdots \tag{5}$$

(repeated indices are summed over). We will proceed as if all of the above matrices had an inverse. This is not true, e.g., $\underline{g}_i$ is singular. We could employ the following device: set $x_i = 1 - \delta$ or δ for $i = A$ or B site and keep δ nonzero until the end of the calculation. This artifact leads to the same conclusions by taking the limit $\delta \to 0$ at the end of the calculation. Further, all quantities are well-behaved in all intermediate steps. Hence, we will proceed with our naive assumption that the matrices are nonsingular. In that case,

$$\underline{G}_{ij}^{-1}(\omega) = \underline{g}_i^{-1}(\omega)\delta_{ij} - \underline{W}_{ij}. \tag{6}$$

If we introduce our effective-medium propagator R as

$$\underline{R}_{ij}^{-1}(\omega) = \omega\underline{I}\,\delta_{ij} - \underline{\sigma}\delta_{ij} - \underline{W}_{ij}, \tag{7}$$

where $\underline{I}$ is the identity matrix and

$$\underline{\sigma} = \begin{bmatrix} \sigma_A & u \\ u & \sigma_B \end{bmatrix} \tag{8}$$

is, for the moment, an arbitrary function of the energy, then

$$\underline{G}_{ij}^{-1} = \underline{R}_{ij}^{-1} - \underline{v}_i\delta_{ij}, \tag{9}$$

where

$$\underline{v}_i = \begin{bmatrix} \omega - \sigma_A - (\omega - \epsilon_A)/x_i & -u \\ -u & \omega - \sigma_B - (\omega - \epsilon_B)/y_i \end{bmatrix}. \tag{10}$$

Equivalently,

$$\underline{G}_{ij} = \underline{R}_{ij} + \underline{R}_{ii}\underline{v}_i\underline{R}_{ij} + \cdots. \tag{11}$$

We now introduce the single-site T matrix τ and full T matrix T as follows:

$$\underline{\tau}_n \equiv \underline{v}_n + \underline{v}_n\underline{R}_{nn}\underline{v}_n + \underline{v}_n\underline{R}_{nn}\underline{v}_n\underline{R}_{nn}v_n + \cdots = (\underline{I} - \underline{v}_n\underline{R}_{nn}^{-1})\underline{v}_n, \tag{12}$$

$$\underline{T}_n \equiv \underline{\tau}_n + \sum_{m\neq n}\underline{\tau}_n\underline{R}_{nm}\underline{\tau}_m + \underline{\tau}_n\sum_{m\neq n}\underline{R}_{nm}\underline{\tau}_m\sum_{p\neq m}\underline{R}_{mp}\underline{\tau}_p + \cdots. \tag{13}$$

Then Eq. (11) can be rearranged so that

$$\underline{G}_{ij} = (\underline{R}_{ij} + \underline{R}_{il}\underline{T}_l\underline{R}_{lj}). \tag{14}$$

Up to this point, the treatment has been exact. It follows from Eq. (14) that

$$\langle\underline{G}\rangle = \underline{R} + \underline{R}\langle\underline{T}\rangle\underline{R}, \tag{15}$$

and hence, the effective-medium propagator R is equal to the averaged Green's function $\langle G\rangle$ if and only if the averaged T matrix $\langle T\rangle$ vanishes.

We can re-express $\langle T\rangle$ as

$$\langle\underline{T}_n\rangle = \langle\underline{\tau}_n\rangle\left(\underline{I} + \sum_{m\neq n}\underline{R}_{nm}\langle\underline{T}_m\rangle\right) + \left\langle(\underline{\tau}_n - \langle\underline{\tau}_n\rangle)\sum_{m\neq n}\underline{R}_{nm}(\underline{T}_m - \langle\underline{T}_m\rangle)\right\rangle \tag{16}$$

The single-site approximation[4] is to neglect $\Delta\tau_n\Delta\tau_m$ $m\neq n$, i.e.,

$$\langle\underline{T}_n\rangle \simeq \langle\underline{\tau}_n\rangle\left(\underline{I} + \sum_{m\neq n}\underline{R}_{mn}\langle\underline{T}_m\rangle\right). \tag{17}$$

Hence, if $\langle\underline{\tau}_n\rangle$ vanishes, then $\langle\underline{T}_n\rangle$ also vanishes within the single-site approximation. If we now choose $\underline{R}$ so that $\langle\underline{\tau}_n\rangle$ vanishes, then this sets the desired self-consistency condition on $\underline{\sigma} = \underline{\Sigma}_{\mathrm{CPA}}$.

Explicitly, if we define the diagonal propagator

$$\underline{\gamma} \equiv \underline{R}_{ii} \equiv \begin{bmatrix} \gamma_A & 0 \\ 0 & \gamma_B \end{bmatrix}, \tag{18}$$

and use Eq. (10) and (12)—keeping δ finite in the definition of v_A and v_B, and then taking the limit $\delta \to 0$ in the expressions for τ_A and τ_B—we obtain

$$\tau_A = \begin{bmatrix} (\epsilon_A - \sigma_A)/[1 - \gamma_A(\epsilon_A - \sigma_A)] & 0 \\ 0 & -1/\gamma_B \end{bmatrix}, \tag{19}$$

with a similar expression for $\underline{\tau}_B$. Setting

$$\langle\underline{\tau}\rangle = x\langle\underline{\tau}_A\rangle + (1-x)\langle\underline{\tau}_B\rangle = 0, \tag{20}$$

we obtain the BEB expressions for σ_A and σ_B (see Ref. 4),

$$\sigma_A = \Sigma_A^{\mathrm{CPA}} = \epsilon_A - C_B/\gamma_A, \tag{21a}$$

$$\sigma_B = \Sigma_B^{\mathrm{CPA}} = \epsilon_B - C_A/\gamma_B. \tag{21b}$$

As yet, the off-diagonal component u is undefined. However, we have a physical constraint, to wit: a site cannot be simultaneously an A site and a B site; hence,

$$R_{ii}^{AB} = 0 \tag{22}$$

(which was assumed in the definition of $\underline{\gamma}$). This is the one constraint used to obtain the one unknown u. In summary the matrix CPA solution is

$$\underline{\Sigma}^{\mathrm{CPA}} = \begin{bmatrix} \epsilon_A - C_B/\gamma_A & u \\ u & \epsilon_B - C_A/\gamma_B \end{bmatrix}, \tag{23}$$

where

$$\gamma = \begin{bmatrix} \gamma_A & 0 \\ 0 & \gamma_B \end{bmatrix} = \underline{R}_{ii}, \tag{24}$$

$$\underline{R}_{ij}^{-1} = (\omega \underline{I} - \underline{\Sigma})\,\delta_{ij} - W_{ij}, \tag{25}$$

and u is obtained from the condition

$$R_{ii}^{AB}(\omega) \equiv 0. \tag{26}$$

The simple structure exhibited by Σ^{CPA} has already been noted by Blackman. Specifically, Σ^{CPA} has the form

$$\underline{\Sigma}^{\mathrm{CPA}} = \begin{bmatrix} \Sigma_{A\infty}(\gamma_A) & u \\ u & \Sigma_{B\infty}(\gamma_B) \end{bmatrix}, \tag{27}$$

where

$$\Sigma_{A(B)\infty}(\gamma_{A(B)}) = \lim_{\epsilon_{B(A)} \to \infty} \Sigma_{\mathrm{CPA}}(\gamma), \tag{28}$$

and Σ_{CPA} is the usual scalar CPA mass operator considered as a functional of the diagonal propagator γ. We will find a similar form for the phonon CPA matrix mass operator. The generalizations to CPn are obtained by a suitable n-site decoupling of the matrix T matrix.

III. MATRIX T MATRIX FOR PHONONS

The development for phonons in a disordered lattice is quite similar to the derivation for electrons. The equation of motion for the phonon propagator G is

$$m_{i\alpha}\omega^2 G_{\alpha\beta}(ij) = \delta_{ij}\delta_{\alpha\beta} + \Phi_{\alpha\gamma}(lj), \tag{29}$$

where i labels a unit cell in the Brovais lattice, and α labels the coordinates of B-basis atoms in the unit cell ($\alpha = 1, 2 \ldots, 3B$), and m_i is the corresponding mass. The harmonic approximation is employed. Φ is the dynamical matrix. Again we may introduce a matrix dynamical matrix, propagator and locator, respectively, as follows:

$$\underline{\Phi}_{\alpha\beta}(ij) = \begin{bmatrix} \Phi_{\alpha\beta}^{HH}(ij) & \Phi_{\alpha\beta}^{AD}(ij) \\ \Phi_{\alpha\beta}^{DH}(ij) & \Phi_{\alpha\beta}^{DD}(ij) \end{bmatrix}, \tag{30}$$

$$\underline{G}_{\alpha\beta}(ij) \equiv \begin{bmatrix} x_i x_j G_{\alpha\beta}(ij) & x_i y_j G_{\alpha\beta}(ij) \\ y_i x_j G_{\alpha\beta}(ij) & y_i y_j G_{\alpha\beta}(ij) \end{bmatrix}, \tag{31}$$

$$p_\alpha(i) \equiv \begin{bmatrix} x_i/m_{H\alpha}\omega^2 & 0 \\ 0 & y_i/m_{D\alpha}\omega^2 \end{bmatrix}, \tag{32}$$

where x_i is again a projection operator

$$x_i = 1 - y_i = \begin{cases} 1 & \text{if } i \text{ is the host } (H) \text{ cell,} \\ 0 & \text{if } i \text{ is the defect } (D) \text{ cell,} \end{cases} \tag{33}$$

and $m_{H\alpha}$ ($m_{D\alpha}$) is the mass of the αth atom in basis B when the unit cell corresponds to a host (defect) cell. (Again we will need to redefine $x_i = 1 - \delta$ or δ for intermediate steps and then take the limit $\delta \to 0$.) Note that there is a hidden assumption in Eq. (30), specifically that $\Phi_{\alpha\beta}(ij)$ depends only on the nature of the atoms on the two sites specified and is independent of the environment. This question will not be pursued further in this particular publication.

A matrix equation of motion then follows:

$$\underline{G}_{\alpha\beta}(ij) = \delta_{ij}\delta_{\alpha\beta}\underline{p}_\alpha(i) + \underline{p}_\alpha(i)\,\underline{\Phi}_{\alpha\beta}(ij)\,\underline{p}_\beta(j) + \underline{p}_\alpha(i)\,\Phi_{\alpha\delta}(il)\,\underline{p}_\delta(l)\,\underline{\Phi}_{\delta\beta}(lj)\,\underline{p}_\beta(j) + \cdots, \tag{34}$$

as may be found by performing the indicated matrix multiplications and comparing term by term with Eq. (31). Hence,

$$\underline{G}_{\alpha\beta}^{-1}(ij) = \underline{p}_\alpha^{-1}(i)\,\delta_{\alpha\beta}\delta_{ij} - \underline{\Phi}_{\alpha\beta}(ij). \tag{35}$$

We now introduce the inverse of the effective-medium propagator,

$$\underline{R}_{\alpha\beta}^{-1}(ij) \equiv \omega^2 m_{H\alpha}\delta_{ij}(\delta_{\alpha\beta}\underline{I}) - \underline{\epsilon}_{\alpha\beta} - \underline{\Phi}_{\alpha\beta}(ij). \tag{36}$$

Here $\underline{\epsilon}_{\alpha\beta}$ plays the role of a mass operator. Eventually, we will determine $\underline{\epsilon}$ by the condition that $R = \langle G \rangle$ within a single-cell approximation.

It follows from the above that

$$\underline{G}_{\alpha\beta}^{-1}(ij) = \underline{R}_{\alpha\beta}^{-1}(ij) - \delta_{ij}\,\underline{v}_{\alpha\beta}(i), \tag{37}$$

where

$$\underline{v}_{\alpha\beta}(i) = \begin{bmatrix} \delta_{\alpha\beta} m_{H\alpha}\omega^2(1 - 1/x_i) - \epsilon_{\alpha\beta}^{HH} & -\epsilon_{\alpha\beta}^{HD} \\ -\epsilon_{\alpha\beta}^{DH} & \delta_{\alpha\beta} m_{H\alpha}\omega^2\,[1 - (m_{D\alpha}/m_{H\alpha})(1/y_i)] - \epsilon_{\alpha\beta}^{DD} \end{bmatrix} \tag{38}$$

The development now is an exact parallel of the election case. We obtain within the single-cell approximation $\underline{R} = \langle \underline{G} \rangle$ if $\langle \underline{T}_{\alpha\beta}(i) \rangle = 0$, where $\underline{\tau}_{\alpha\beta}$ plays the role of a single-cell matrix T matrix. Explicitly,

$$\underline{\tau}(i) = \underline{v}(i)\,[\underline{I} - \underline{R}(ii)\,\underline{v}(i)]^{-1}, \tag{39}$$

where the above matrices are actually "double" matrices. Specifically,

$$\underline{v}(i) = [\underline{v}_{\alpha\beta}], \quad \underline{\tau}(i) = [\underline{\tau}_{\alpha\beta}], \quad \text{etc.}$$

The equation $\underline{\tau}(i) = 0$ represents $2[3B]^2$ equations in $2[3B]^2$ unknowns (the $\epsilon_{\alpha\beta}^{HA}$ and $\epsilon_{\alpha\beta}^{DD}$). As in the electron case, in order to determine $\epsilon_{\alpha\beta}^{HD}$ and $\epsilon_{DH}^{\alpha\beta}$, they must be supplemented with the auxiliary conditions $R_{\alpha\beta}^{DH}(ii) = R_{\alpha\beta}^{HD}(ii) = 0$, i.e., a given cell ($i$) cannot be simultaneously a host and a defect cell. The degree of complexity in the equations depends on the dimensionality and on the number of basis atoms.

In one dimension for a monatomic lattice, the above self-consistency equations reduce to three equations in three unknowns (ϵ^{HH}, ϵ^{DD}, $\epsilon^{HD} = \epsilon^{DH}$). There is no restriction on the range of the forces. In three dimensions, monatomic lattice, simple cubic symmetry, and forces restricted to nearest

neighbors (so that $\Phi_{\alpha\beta}=0$ for $\alpha\neq\beta$ and $\Phi_{11}=\Phi_{22}=\Phi_{33}$), there are three equations in three unknowns. In either of these cases an explicit solution may be obtained after some matrix manipulations.

The results are summarized by the following equations. The effective-medium propagator is

$$\underline{R}(ij)\equiv\begin{bmatrix}R^{HH}(ij) & R^{HD}(ij)\\ R^{DH}(ij) & R^{DD}(ij)\end{bmatrix}, \tag{40}$$

$$\underline{R}^{-1}(ij)=\omega^2 m_H\delta_{ij}[\underline{I}-\underline{\epsilon}^{\mathrm{CPA}}-\underline{\Phi}(ij)] \tag{41}$$

(m_H is mass of an atom on a host site), and

$$\underline{\epsilon}^{\mathrm{CPA}}=\begin{bmatrix}\epsilon^{HH} & \epsilon^{HD}\\ \epsilon^{HD} & \epsilon^{DD}\end{bmatrix}, \tag{42}$$

where

$$\epsilon^{HH}=-c/\gamma_H, \tag{43a}$$

$$\epsilon^{DD}=-(1-c)/\gamma_D+\Delta m\omega^2, \tag{43b}$$

and ϵ^{HD} is determined by the condition

$$R^{HD}(ij)=0. \tag{44}$$

In the above equations, c is the concentration of host sites, $\Delta m=m_H-m_D$, and $\gamma_H=R^{HH}_{(ii)}$, $\gamma_D=R^{DD}_{(ii)}$. As in the electron case, ϵ^{HH} and ϵ^{DD} (aside from the mass-splitting term) have the form of the CPA mass operator in the infinite-mass limit.

IV. CONCLUSION

We have demonstrated that the coherent-potential approximation can be extended to include off-diagonal randomness in a simple fashion, both formally and practically, by the replacement of scalar quantities by matrices in an appropriate manner. It is hoped that this will encourage investigators to include this important extension in future modeling of disordered systems.

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