Electronic structure of random alloys by the linear band-structure methods

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We present a new method for the determination of the electronic structure of random transitionmetal alloys, which combines the simplicity of empirical tight-binding schemes with the accuracy of the first-principles treatments. Our method uses the first-principles tight-binding linear muffin-tin orbitals description of the electronic states and the coherent-potential approximation to describe the effect of disorder. The central result of our theory is the expression for the configurationally averaged Green's-function matrix, which is then used to evaluate various one-electron properties of random alloys. The separation of structural and atom-dependent features in our theory allows us to include properly the effect of different positions, widths, and shapes of the band structures of individual alloy constituents. Our theory includes the charge self-consistency and lattice-relaxation effects in an approximate, yet accurate way and it represents a simple alternative to the fully self-consistent treatment.

I. INTRODUCTION

The linear muffin-tin orbitals (LMTO) description of electron states in band theory introduced a decade ago by Andersen¹ has led to development of very efficient firstprinciples computational schemes based on the Hohenberg-Kohn density-functional formalism for the self-consistent determination of the band structure of solids.

The most noticeable features of the LMTO formalism² are the following: (i) The description of metals, including the transition metals, as well as semiconductors and insulators on equal footing. (ii) The LMTO basis set is minimal, i.e., only one s orbital, three p orbitals, five d orbitals, etc., are needed for an accurate description of electron states in solids. (iii) The LMTO orbital centered at a given site may be expanded about other sites in terms of radial functions, spherical harmonics, and structure constants. Within the atomic-sphere approximation (ASA), according to which the Wigner-Seitz (WS) cells are substituted by slightly overlapping WS spheres, this leads to a factorization of the matrix elements of a given operator into products of structure constants and radial integrals. (iv) The original, infinite-ranged LMTO basis set can be transformed exactly³ into new basis sets, called muffintin-orbital (MTO) representations, with varying degrees of localization in the real space. (v) The LMTO set is complete for the muffin-tin (MT) potential used in its definition, but it can be used also to treat potentials other than MT ones.

The especially simple, yet very accurate description of the electronic structure of solids is obtained^{2,3} within the so-called orthogonal MTO representation in the ASA. Starting from first principles, one may construct the tight-binding (TB) Hamiltonian, whose hopping integrals factorize into potential parameters and canonical structure constants, describing, respectively, the scattering properties of atoms and the geometry of the lattice. Of great importance is the existence of a simple scaling relation connecting the Green's functions (GF) in the orthogonal and in any other MTO representation. This scaling property can be conveniently used if one applies the LMTO description to the study of such complicated systems as disordered alloys, both metallic⁴ and semiconductor,⁵ or solid surfaces and interfaces.⁶

It is the purpose of this paper to discuss in detail the application of the LMTO formalism to the evaluation of the electronic structure of disordered binary transitionmetal alloys within the coherent-potential approximation (CPA) originally due to Soven and Taylor. The resulting formalism has the simplicity and physical transparency of empirical TB-CPA schemes, while it retains the accuracy of the first-principles Korringa-Kohn-Rostoker (KKR) CPA approach. The separation of structural and atomdependent properties allows us to perform the CPA averaging without limitations inherent to empirical TB-CPA approaches. In addition, we shall demonstrate how the flexibility in the choice of sizes of the WS spheres in random binary alloys makes possible approximate, yet accurate and consistent, treatment of charge selfconsistency and lattice-relaxation effects.

The central result of our paper is the expression for the configurationally averaged one-electron GF matrix from which various physical properties of random alloys can be determined. The paper elaborates in detail and further generalizes the ideas developed in a recent paper.⁴

The paper is organized as follows. In Sec. II we briefly review the LMTO method in a form suitable for further development and in order to establish notation. The central part of the paper is Sec. III, in which we give the expression for the GF matrix configurationally averaged within the CPA. The explicit expressions for evaluation of various physical quantities are presented in Sec. IV. The approximate inclusion of the effects of charge selfconsistency and lattice relaxations is discussed in Sec. V, while in Sec. VI we present the computational aspects of the theory. Conclusions and additional comments are given in the last section.

II. THE TB-LMTO FORMALISM

In this section we briefly review the TB-LMTO formalism in order to introduce notation and formulas neces-

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sary for application of the theory to random alloys. For further details, we refer the reader to a comprehensive review of the LMTO approach in Ref. 2.

A. Muffin-tin orbitals (MTO) and their representations

The energy-independent muffin-tin orbital $\chi^{\alpha}_{RL}(r_R)$ with collective angular momentum index L = (lm) centered at the lattice site R and corresponding to a general MTO representation α is

$$\chi_{RL}^{\alpha}(r_{R}) = \varphi_{RL}(r_{R}) + \sum_{R',L'} \dot{\varphi}_{R'L'}^{\alpha}(r_{R'})h_{R'L',RL}^{\alpha} + K_{RL}^{\alpha,i}(r_{R}) ,$$

$$\dot{\varphi}_{RL}^{\alpha}(r_{R}) = \dot{\varphi}_{RL}(r_{R}) + \varphi_{RL}(r_{R})o_{RL}^{\alpha} .$$
(1a)

Here, $\varphi_{RL}(r_R) = \varphi_{RL}(\kappa_R) Y(\hat{r}_R)$, where $r_R = r - R$, $\kappa_R = |r_R|$, and $\hat{r}_R = r_R / \kappa_R$, and Y_L is the spherical harmonics. The function $\varphi_{RL}(r_R)$ is the solution of the radial scalar-relativistic Schrödinger equation for the spherically averaged one-electron solid-state potential $V_R(r_R)$ determined within the density-functional formalism and calculated at the energy E_{vRL} . Similarly, $\dot{\varphi}_{RL}(r_R)$ is the energy derivative of φ_{RL} for the same energy. The energy E_{vRL} is usually chosen in the middle of the energy interval of interest. The function of φ_{RL} is normalized to unity in its sphere of the radius s_R centered at R: $\int_{0}^{3_{R}} \varphi_{RL}^{2}(\kappa_{R}) \kappa_{R}^{2} d\kappa = 1.$ The quantity σ_{RL}^{α} is the overlap of φ_{RL} and $\dot{\varphi}_{RL}^{\alpha}$, $o_{RL}^{\alpha} = \langle \varphi_{RL} | \dot{\varphi}_{RL}^{\alpha} \rangle$. Another parameter to be used is $p_{RL} = \langle \dot{\varphi}_{RL} | \dot{\varphi}_{RL} \rangle$, which turns out to be the small parameter of a linear method. The function $K_{RL}^{\alpha,i}(r_R)$ is the contribution to the MTO coming from the interstitial region. The matrix $h_{RL,R'L'}^{\alpha}$ is determined in such a way that the wave function [Eq. (1a)] is continuous and differentiable on the sphere boundary at each sphere. Its explicit form is

$$h_{RL,RL'}^{\alpha} = (c_{RL}^{\alpha} - E_{\nu RL}) \delta_{RR'} \delta_{LL'} + (\Delta_{RL}^{\alpha})^{1/2} S_{RL,R'L'}^{\alpha} (\Delta_{RL'}^{\alpha})^{1/2} , \qquad (1b)$$

where $S_{RL,R'L'}^{\alpha}$ are the matrix elements of the structure constant S^{α} in the MTO representation α , and Δ^{α} and c^{α} are the so-called potential parameters, which can be, as well as o^{α} , expressed via the potential function P_{RL}^{α} evaluated at the energy E_{vRL} , and its first \dot{P}_{RL}^{α} and second \ddot{P}_{RL}^{α} energy derivative at the same energy in the following manner:

$$(\Delta_{RL}^{\alpha})^{1/2} = \dot{P}_{RL}^{\alpha}(E_{\nu RL}) ,$$

$$c_{RL}^{\alpha} - E_{\nu RL} = -P_{RL}^{\alpha}(E_{\nu RL})[\dot{P}_{RL}^{\alpha}(E_{\nu RL})]^{-1} , \qquad (2)$$

$$o_{RL}^{\alpha} = \ddot{P}_{RL}^{\alpha}(E_{\nu RL})[2\dot{P}_{RL}^{\alpha}(E_{\nu RL})]^{-1} .$$

Below we often drop indices R and L, and use the matrix notation for simplicity of writing. For example, the quantities P_{RL}^{α} and $S_{RL,R'L'}^{\alpha}$ are elements of the diagonal matrix P^{α} and the matrix S^{α} , respectively.

The structure constant S^{α} and the potential function $P^{\alpha}(E)$, which enter the definition of MTO's, play a central role in the LMTO theory. We shall discuss their properties in some detail. The potential functions $P^{\alpha}_{RL}(E)$ are expressed in terms of conventional potential

functions $P_{RL}^0(E)$ and the elements α_{RL} of the diagonal matrix α defining the MTO representation α ,

$$P_{RL}^{\alpha}(E) = P_{RL}^{0}(E) [1 - \alpha_{RL} P_{RL}^{0}(E)]^{-1} .$$
(3)

The quantities $P_{RL}^0(E)$ have direct physical meaning: they are proportional to cotangents of the phase shifts related to the solid-state potential $V_R(r_R)$ in a sphere at R. The potential functions $P_{RL}^0(E)$ can be parametrized over a broad range of energies in terms of potential parameters describing the positions C_{RL} , the widths Δ_{RL} , and the distortions γ_{RL} of the "pure" RL bands:

$$P_{RL}^{0}(E) = (E - C_{RL}) [\Delta_{RL} + \gamma_{RL} (E - C_{RL})]^{-1} .$$
(4)

The potential parameters are elements of diagonal matrices C, Δ , and γ and, via P^0 and P^{α} , they characterize the scattering properties of atoms placed at lattice sites. Using Eqs. (3) and (4), we express the potential function in the MTO representation α via the potential function of any other MTO representation, say β , as

$$P_{RL}^{\alpha}(E) = P_{RL}^{\beta}(E) [1 - (\alpha_{RL} - \beta_{RL}) P_{RL}^{\beta}(E)]^{-1} .$$
 (5)

The geometry of the lattice sites enters the theory via the structure constant S^{α} which is expressed via the canonical structure constant S^{0} , known analytically as

$$S_{RL,R'L'}^{\alpha} = [S^{0}(1 - \alpha S^{0})^{-1}]_{RL,R'L'}.$$
(6)

The elements $S^0_{RL,R'L'}$ depend only on R/w and R'/w, where R and R' are the atomic positions, and w is the average WS radius of a solid. The structure constant S^0 depends only on the geometrical arrangement of the lattice sites, but not on their occupancy by atoms of varying type. Here we shall assume an ideal periodic lattice randomly occupied by atoms A and B. Consequently, the structure constant S^0 is nonrandom. The effect of possible structural distortions due to the lattice relaxations will be discussed in Sec. V. The quantities $S_{RL,R'L'}^0$ behave like $(w/d)^{l+l'+1}$, where d = |R - R'|. For low orbital indices, l = 0 or 1, S^0 is thus long ranged in the real space. On the contrary, the elements $S^{\alpha}_{RL,R'L'}$ of the matrix S^{α} , behave like $\exp(-\lambda_{ll'}^{\alpha}d/w)$, with $\lambda_{ll'}^{\alpha}$ depending on the choice of the MTO representation α . It has been found that for close-packed lattices the MTO representation β , which is site independent but *l* dependent and specified by values

$$\beta_s = 0.3485, \ \beta_p = 0.0530, \ \beta_d = 0.00107, \ \text{and} \ \beta_l = 0$$

for $l > 2$, (7)

gives the fastest and essentially monotonic decay in the real space. In practice, S^{β} vanishes beyond the secondnearest-neighbor shell for close-packed lattices. Consequently, the MTO's χ^{β}_{RL} are strongly localized in real space contrary to the infinitely ranged conventional MTO's, χ^{0}_{RL} , with $\alpha_{RL} = 0$.

Similarly to (6), we can express S^{α} in terms of S^{β} as

$$S_{RL,R'L'}^{\alpha} = \{ S^{\beta} [1 - (\alpha - \beta) S^{\beta}]^{-1} \}_{RL,R'L'} .$$
 (8)

This form, expressing S^{α} via the most localized S^{β} , is frequently used in applications.⁴⁻⁶

B. Hamiltonian

The scalar-relativistic Schrödinger equation for a solid is solved by seeking the wave function $\psi^{\alpha}(r)$ as a linear combination $\sum_{R,L} \chi^{\alpha}_{RL}(r_R) u^{\alpha}_{RL}$ of the MTO's which form a basis set of conventional variational principles. The eigenvectors u^{α}_{RL} and eigenenergies E are found to be a solution of the eigenvalue problem:²

$$\sum_{R,L} (H_{R'L',RL}^{\alpha} - EO_{R'L',RL}^{\alpha}) u_{RL}^{\alpha} = 0 .$$
 (9a)

The overlap $O_{RL,R'L'}^{\alpha} = \langle \chi_{RL}^{\alpha} | \chi_{R'L'}^{\alpha} \rangle$ and Hamiltonian $H_{RL,R'L'}^{\alpha} = \langle \chi_{RL}^{\alpha} | [-\nabla^2 + V(r)] | \chi_{R'L'}^{\alpha} \rangle$ matrices are evaluated straightforwardly, because involved functions φ_{RL} and $\dot{\varphi}_{RL}$ are nonzero only in their own spheres. The result,^{2,3} in matrix notation, is

$$O^{\alpha} = (1 + h^{\alpha}o^{\alpha})(o^{\alpha}h^{\alpha} + 1) + h^{\alpha}ph^{\alpha} + \langle K^{\alpha,i} | K^{\alpha,i} \rangle ,$$

$$H^{\alpha} = h^{\alpha}(1 + o^{\alpha}h^{\alpha}) + (1 + h^{\alpha}o^{\alpha})E_{\nu}(o^{\alpha}h^{\alpha} + 1) + h^{\alpha}E_{\nu}ph^{\alpha} + \langle K^{\alpha,i} | [-\nabla^{2} + V^{i}(r)] | K^{\alpha,i} \rangle .$$
(9b)

Here, the matrix h^{α} is defined in (1); o^{α} , E_{ν} , and p denote the diagonal matrices with elements o_{RL}^{α} [Eq. (2)], $E_{\nu RL}$, and p_{RL} . Finally $V^{i}(r) = V(r) - \sum_{R} V_{R}(r_{R})$ is the interstitial, nonspherical part of the solid-state potential and the last terms in O^{α} and H^{α} , coming from the interstitial region, are called "combined-correction" terms.^{2,3}

The solution of the eigenvalue problem, Eqs. (9), can be significantly simplified in the ASA, which is the central approximation adopted in this paper. In the MT approximation the interstitial region is poorly treated because the real potential is not flat here. The simplest way to get rid of the interstitial region is the ASA, which consists of replacing the MT spheres by the WS spheres in all formulas. It has been proved that the ASA gives an accurate description of the electronic structure provided that²

$$|s_R + s_{R'} - d| / d < 0.3, \quad d = |R - R'|$$
(10)

where d is the distance of neighboring WS spheres of radii s_R and $s_{R'}$. The close-packed (fcc, bcc, or hcp) transition metals fulfill this condition very well. The fact that the charge distribution can change in all space together with the flexibility in the choice of the WS radii of species in random alloys are important advantages of the ASA to be exploited in Sec. V. Within the ASA, the last terms in O^{α} and H^{α} vanish. We note that the majority of the existing LMTO calculations for various solids have been performed in the ASA. The ASA results for transition metals and band energies up to 0.5 Ry above the Fermi energy nearly coincide with those based on the full LMTO expressions [Eqs. (9)].

The quantities p_{RL} turn out to be small parameters^{2,7} of the LMTO theory and their neglect still allows us to perform fairly accurate band-structure calculations (with an error not exceeding 1% of the bandwidth, i.e., approximately 5 mRy for d bands). We thus obtain, within the ASA,

$$O^{\alpha} = (1 + h^{\alpha} o^{\alpha}) (o^{\alpha} h^{\alpha} + 1) ,$$

$$H^{\alpha} = h^{\alpha} (1 + o^{\alpha} h^{\alpha}) + (1 + h^{\alpha} o^{\alpha}) E_{\nu} (o^{\alpha} h^{\alpha} + 1) .$$
(11)

An especially simple form is obtained in the sitedependent MTO representation γ , $\alpha_{RL} = \gamma_{RL}$, i.e., when α_{RL} 's are given by one of the potential parameters. Then $c_{RL}^{\alpha} = C_{RL}$, $\Delta_{RL}^{\alpha} = \Delta_{RL}$, and $o_{RL}^{\alpha} = 0$, so that

$$H^{\alpha}_{RL,R'L'} = C_{RL} \delta_{RR'} \delta_{LL'} + \Delta^{1/2}_{RL} S^{\gamma}_{RL,R'L'} \Delta^{1/2}_{R'L'}$$

$$O^{\gamma}_{RL,R'L'} = \delta_{RR'} \delta_{LL'} , \qquad (12)$$

$$S^{\gamma}_{RL,R'L'} = [S^{0}(1 - \gamma S^{0})^{-1}]_{RL,R'L'} .$$

There is no overlap; hence the MTO representation γ is called the orthogonal representation. Note, that the eigenvalue problem (9a) leads to the same spectrum for any choice of the MTO representation α . The Hamiltonian (12), specified to the case of the random alloy $A_x B_{1-x}$, is the starting point in the forthcoming development. Its properties can be summarized as follows: (i) It is firstprinciples, with hoppings factorizing into structure constants characterizing the geometry of the lattice and the potential parameters characterizing the scattering potentials in WS spheres, and obtained from the solutions of the radial scalar-relativistic Schrödinger equation there. (ii) It describes the valence states with accuracy comparable to the KKR method or to any other first-principles approach. (iii) Contrary to the empirical TB Hamiltonians, it describes properly not only variations in atomic levels due to alloying, but also the variations in bandwidths and shapes of alloy species just as the KKR-CPA method does. In addition, the element $H_{RL,R'L'}^{\gamma,AB}$ between the site R occupied, e.g., by atom A and the site R' occupied by atom B, which is unknown in the empirical TB method, is also given by (12). It even depends on the occupation of all other sites than R and R' via the random quantity γ . (iv) The separation of structural and atomdependent parts of H^{γ} , mentioned above and inherent in the ASA, allows us to perform the CPA averaging without any constraints common to other TB-CPA approaches.

C. Green's functions

For random alloys, the proper quantity to be evaluated is the configurationally averaged one-electron GF. With the help of this, any physical quantity of interest can be determined. The GF corresponding to the Hamiltonian (12) is

$$G_{RL,R'L'}(z) = (z \, \mathbb{1} - H^{\gamma})_{RL,R'L'}^{-1}$$

= $\Delta_{RL}^{-1/2} [(P^{\gamma}(z) - S^{\gamma})^{-1}]_{RL,R'L'} \Delta_{R'L'}^{-1/2} .$ (13)

Here, 1 denotes the unit operator, z is the energy in the complex energy plane, and $P^{\gamma}(z) = (z - C)/\Delta$ is the potential function in the MTO representation γ [see Eqs. (3) and (4)]. Using the relation between GF's in different MTO representations valid in the ASA,⁸ we express G(z) in the general MTO representation α as

$$G_{RL,R'L'}(z) = \lambda_{RL}^{\alpha}(z)\delta_{RR'}\delta_{LL'} + \mu_{RL}^{\alpha}(z)g_{RL,R'L'}^{\alpha}(z)\mu_{R'L'}^{\alpha}(z) ,$$

$$g_{RL,R'L'}^{\alpha}(z) = \{ [P^{\alpha}(z) - S^{\alpha}]^{-1} \}$$

$$\begin{aligned} &\chi_{RL}^{\alpha}(z) = (\gamma_{RL} - \alpha_{RL}) \mu_{RL}^{\alpha}(z) / \Delta_{RL}^{1/2} , \\ &\chi_{RL}^{\alpha}(z) = [\dot{P}_{RL}^{\alpha}(z)]^{1/2} \\ &= \Delta_{RL}^{1/2} / [\Delta_{RL} + (\gamma_{RL} - \alpha_{RL})(z - C_{RL})] . \end{aligned}$$
(14)

The structure constant S^{α} , Eq. (6), is generally random in alloys. There are, however, two important exceptions: the canonical MTO representation, $\alpha_{RL} = 0$, and the most-localized MTO representation $\alpha_{RL} = \beta_L$ [Eq. (7)]. These nonrandom MTO representations will play a central role in the alloy theory to be developed in this paper.

III. THE COHERENT-POTENTIAL APPROXIMATION

In this section we shall perform the configurational averaging of the GF of random alloys, (14), within the CPA. In a binary alloy $A_x B_{1-x}$, characterized by the Hamiltonian (12), the site-diagonal potential parameters X_{RL} , X = C, Δ , and γ , randomly take on two different values, X_L^A with the probability $c^A = x$, and X_L^B with the probability $c^B = 1 - x$. Due to random Δ_{RL} and γ_{RL} , the hoppings $H_{RL,R'L'}^{\gamma}$, (12), have a complicated off-diagonal randomness. Consequently, the CPA, which can treat only the site-diagonal disorder, cannot be applied to G(z)in the form (13). The remedy is to express G(z) in the form (14) with $\alpha_{RL} \equiv \beta_L$, i.e., to go over to the nonrandom most-localized MTO representation, independent of the occupation of sites by atoms [see Eq. (7)]. The structure constant $S_{RL,R'L'}^{\beta}$ is then nonrandom, and the random quantities $P_{RL}^{\beta}(z)$, $\lambda_{RL}^{\beta}(z)$, and $\mu_{RL}^{\beta}(z)$, which enter the definition of G(z), are all site-diagonal quantities. They are expressed via the potential parameters, and consequently randomly take on two different values $P_L^{\beta,Q}(z)$, $\lambda_L^{\beta,Q}(z)$, and $\mu_L^{\beta,Q}(z)$ with probabilities c^Q , Q = A or B. We introduce the occupation index η_R^Q ; $\eta_R^Q = 1$ if an atom of the type Q is at the site R, and $\eta_R^Q = 0$ otherwise. The configurational average of $G_{RL,R'L'}(z)$, $\langle G(z) \rangle_{RL,R'L'}$, is expressed as

$$\langle G(z) \rangle_{RL,R'L'} = \sum_{Q} \lambda_{L}^{\beta,Q}(z) \langle \eta_{R}^{Q} \rangle \delta_{RR'} \delta_{LL'} + \sum_{Q,Q'} \mu_{L}^{\beta,Q}(z) \langle g^{\beta}(z) \rangle_{RL,R'L'}^{QQ'} \mu_{L'}^{\beta,Q'}(z) ,$$
(15)

$$\langle g^{\beta}(z) \rangle_{RL,R'L'}^{QQ'} = \langle \eta_R^Q g^{\beta}_{RL,R'L'}(z) \eta_R^{Q'} \rangle \text{ with } Q, Q' = A, B$$

The site-diagonal term, proportional to η_R^Q , averages trivially,

$$\sum_{Q} \lambda_{L}^{\beta,Q}(z) \langle \eta_{R}^{Q} \rangle = \sum_{Q} c^{Q} \lambda_{L}^{\beta,Q}(z) .$$
⁽¹⁶⁾

The evaluation of $\langle g^{\beta}(z) \rangle^{QQ'}$ is nontrivial, and the details are given in the Appendix. The result is

$$\langle g^{\beta}(z) \rangle_{RL,R'L'}^{QQ'} = \frac{\operatorname{sgn}(Q,Q')}{\Delta P_{L}^{\beta}(z) \Delta P_{L'}^{\beta}(z)} \{ [P_{L}^{\beta,\overline{Q}}(z) - \mathcal{P}_{L}^{\beta}(z)] \langle g^{\beta}(z) \rangle_{RL,R'L'} [P_{L}^{\beta,\overline{Q}'}(z) - \mathcal{P}_{L'}^{\beta}(z)] + [\langle P_{L}^{\beta}(z) \rangle - \mathcal{P}_{L}^{\beta}(z)] \delta_{RR'} \delta_{LL'} \} .$$

$$(17)$$

Here, $\langle P_L^{\beta}(z) \rangle = \sum_Q c^Q P_L^{\beta,Q}(z), \quad \Delta P_L^{\beta}(z) = P_L^{\beta,A}(z)$ $-P_L^{\beta,B}(z), \text{ and } \operatorname{sgn}(Q,Q') = 1 \text{ for } Q = Q', \text{ and } \operatorname{sgn}(Q,Q')$ $= -1 \text{ for } Q \neq Q', \text{ while } Q, Q' = A \text{ or } B.$ The meaning of \overline{Q} or \overline{Q}' is $\overline{Q} = B$ if Q = A, and $\overline{Q} = A$ if Q = B, and similarly for \overline{Q}' . The quantity $\langle g^{\beta}(z) \rangle_{RL,R'L'}$ is

$$\langle g^{\beta}(z) \rangle_{RL,R'L'} = \{ [\mathcal{P}^{\beta}(z) - S^{\beta}]^{-1} \}_{RL,R'L'} .$$
⁽¹⁸⁾

The coherent-potential function $\mathcal{P}^{\beta}(z)$ is, for cubic lattices, a site- and symmetry-diagonal matrix with elements $\mathcal{P}_{L}^{\beta}(z)$, and it is determined from a set of coupled CPA equations:

$$\mathcal{P}_{L}^{\beta}(z) = \langle P_{L}^{\beta}(z) \rangle + [P_{L}^{\beta,A}(z) - \mathcal{P}_{L}^{\beta}(z)] \Phi_{L}^{\beta}(z) \\ \times [P_{L}^{\beta,B}(z) - \mathcal{P}_{L}^{\beta}(z)] , \qquad (19)$$

$$\Phi_L^{\beta}(z) = \frac{1}{N} \sum_k \{ [\mathcal{P}^{\beta}(z) - S^{\beta}(k)]^{-1} \}_{LL} .$$
 (20)

Finally, the quantity $S_{LL'}^{\beta}(k)$ is the Bloch transform of $S_{RL,R'L'}^{\beta}$. Alternatively, the CPA equations can be put into other forms useful in applications, namely

$$\sum_{Q} c \,^{Q} \tau_{L}^{\beta,Q}(z) = 0 ,$$

$$\tau_{L}^{\beta,Q}(z) = \frac{P_{L}^{\beta,Q}(z) - \mathcal{P}_{L}^{\beta}(z)}{1 + [P_{L}^{\beta,Q}(z) - \mathcal{P}_{L}^{\beta}(z)] \Phi_{L}^{\beta}(z)} ,$$
(19')

or

$$\begin{split} \Phi_{L}^{\beta}(z) &= \sum_{Q} c^{Q} \Phi_{L}^{\beta,Q}(z) , \\ \Phi_{L}^{\beta,Q}(z) &= \Phi_{L}^{\beta}(z) \{ 1 + [P_{L}^{\beta,Q}(z) - \mathcal{P}_{L}^{\beta}(z)] \Phi_{L}^{\beta}(z) \}^{-1} , \\ \Phi_{L}^{\beta,Q}(z) &= [P_{L}^{\beta,Q}(z) - \Omega_{L}^{\beta}(z)]^{-1} , \end{split}$$

$$(19^{\prime\prime})$$

$$\Omega_{L}^{\beta}(z) &= \mathcal{P}_{L}^{\beta}(z) - [\Phi_{L}^{\beta}(z)]^{-1} . \end{split}$$

The quantity $\tau_L^{\beta,Q}(z)$ is easily recognized as the *T* matrix for the "potential" $P_L^{\beta,Q}(z)$ embedded in the effective medium characterized by $\mathcal{P}_L^{\beta}(z)$, while $\Omega_L^{\beta}(z)$ is the coherent interactor to be discussed in Sec. IV. The CPA equations can be thus considered as equations for unknown quantities $\mathcal{P}_L^{\beta}(z)$ or $\Omega_L^{\beta}(z)$.

The following remarks are now in order: (i) In the low-concentration limit, $c_A \rightarrow 0$, we obtain from (19)

$$\mathcal{P}_{L}^{\beta}(z) = P_{L}^{\beta,B}(z) + c^{A} \tau_{L}^{\beta,imp}(z) ,$$

$$\tau_{L}^{\beta,imp}(z) = \frac{\Delta P_{L}^{\beta}(z)}{1 + \Delta P_{L}^{\beta}(z) \Phi_{L}^{\beta(0)}(z)} ,$$
(21)

$$\Phi_{L}^{\beta(0)}(z) = \frac{1}{N} \sum_{k} \{ [P^{\beta,B}(z) - S^{\beta}(k)]^{-1} \}_{LL} .$$

The quantity $\tau_L^{\beta,\text{imp}}(z)$ is the *T* matrix corresponding to the impurity "potential" $\Delta P_L^{\beta}(z) = P_L^{\beta,A}(z) - P_L^{\beta,B}(z)$. Our result coincides with that obtained from the LMTO-ASA Green's-function method⁹ for the single impurity. Note, however, that due to the CPA, the impurity perturbation is limited to the impurity site in our theory. (ii) The theory can be formulated also in the MTO representation $\alpha_{RL} = 0$, which is also nonrandom. In this case, as explained in Sec. II, the matrix $S_{LL,R'L'}^0$ is long ranged in real space, and the evaluation of $S_{LL'}^{0}(k)$ is complex, requiring the Ewald summation.¹⁰ On the contrary, in the MTO representation β , (7), the matrix $S_{LL'}^{\beta}(k)$ is evaluated straightforwardly using the Slater-Koster tables,¹¹ or, even more directly, the tabulated values of $S_{RL,R'L'}^{\beta}$ matrix elements.¹² (iii) For noncubic lattices, e.g., for the hexagonal lattice, the related quantities $\mathcal{P}^{\beta}(z)$, $\Phi^{\beta}(z)$, and $\Omega^{\beta}(z)$, are nondiagonal matrices with respect to indices L

and L' (see the Appendix). On the contrary, for cubic fcc and bcc lattices, these matrices are diagonal with respect to L and L'. For all lattices, however, these quantities are diagonal with respect to the site index R in the CPA. In cubic lattices, out of nine elements $\mathcal{P}^{\beta}_{L}(z)$ only four are independent, namely $\mathcal{P}^{\beta}_{s}(z)$ (L=s), $\mathcal{P}^{\beta}_{p}(z)$ (L=x,y,z), $\mathcal{P}^{\beta}_{l_{2g}}(z)$ (L=xy,yx,zx), and $\mathcal{P}^{\beta}_{e_{g}}(z)$ $(L=x^{2}-y^{2}, 3z^{2}-1)$.

Using Eqs. (15) and (17), we can put $\langle G(z) \rangle_{RL,R'L'}$ into another more compact form,⁴

$$\langle G(z) \rangle_{RL,R'L'} = \Lambda_L^\beta(z) \delta_{RR'} \delta_{LL'} + M_L^\beta(z) \langle g^\beta(z) \rangle_{RL,R'L'} M_{L'}^\beta(z) , \qquad (22) \langle g^\beta(z) \rangle_{RL,R'L'} = \{ [\mathcal{P}^\beta(z) - S^\beta]^{-1} \}_{RL,R'L'} .$$

In these equations

$$\Lambda_{L}^{\beta}(z) = \langle \lambda_{L}^{\beta}(z) \rangle + [\Delta \mu_{L}^{\beta}(z)]^{2} [\langle P_{l}^{\beta}(z) \rangle - \mathcal{P}_{L}^{\beta}(z)] / [\Delta P_{L}^{\beta}(z)]^{2} ,$$

$$M_{L}^{\beta}(z) = \{ \mu_{L}^{\beta,A}(z) [P_{L}^{\beta,B}(z) - \mathcal{P}_{L}^{\beta}(z)] - \mu_{L}^{\beta,B}(z) [P_{L}^{\beta,A}(z) - \mathcal{P}_{L}^{\beta}(z)] \} / \Delta P_{L}^{\beta}(z) ,$$
(23)

and we have denoted $\langle X_L \rangle = \sum_Q c^Q X^Q$, $X_L^Q = \lambda_L^{\beta,Q}(z)$, $P_L^{\beta,Q}(z)$ and $\Delta X_L = X_L^A - X_L^B$, $X_L^Q = \mu_L^{\beta,Q}(z)$, $P_L^{\beta,Q}(z)$. The Bloch transform of (22) is

$$\langle G(k,z) \rangle_{LL'} = \Lambda_L^{\beta}(z) \delta_{LL'} + M_L^{\beta}(z) \langle g^{\beta}(k,z) \rangle_{LL'} M_{L'}^{\beta}(z) ,$$

$$\langle g^{\beta}(k,z) \rangle_{LL'} = \{ [\mathcal{P}^{\beta}(z) - S^{\beta}(k)]^{-1} \}_{LL'} .$$

$$(24)$$

Equations (22) or (24), for the configurationally averaged GF in the site or Bloch representations, are the central result of our paper. Any one-electron property related to random alloys can be determined from the configurationally averaged GF.

To put (22) into a physically more transparent form, we introduce new quantities $\tilde{C}(z)$, $\tilde{\Delta}(z)$, and $\tilde{\gamma}(z)$, diagonal in the site and orbital indices, by the relations

$$\Lambda_{L}^{\beta}(z) = [\tilde{\gamma}_{L}(z) - \beta_{L}] \mathcal{D}_{L}^{\beta}(z) ,$$

$$M_{L}^{\beta}(z) = \tilde{\Delta}_{L}^{1/2}(z) \mathcal{D}_{L}^{\beta}(z) ,$$

$$\mathcal{P}_{L}^{\beta}(z) = [z - \tilde{C}_{L}(z)] \mathcal{D}_{L}^{\beta}(z) ,$$

$$\mathcal{D}_{L}^{\beta}(z) = \mathcal{P}_{L}^{\beta}(z) \Lambda_{L}^{\beta}(z) - [M_{L}^{\beta}(z)]^{2} .$$
(25)

An important identity,

$$1/\mathcal{D}_{L}^{\beta}(z) = \widetilde{\Delta}_{L}(z) + [\widetilde{\gamma}_{L}(z) - \beta_{L}][z - \widetilde{C}_{L}(z)], \qquad (26)$$

immediately follows from (25). Using basically the same algebra as employed in Ref. 8 to derive the identity (91), we find that $\langle G(z) \rangle = [z \mathbb{1} - H^{\text{eff}}(z)]^{-1}$, where

$$H_{RL,R'L'}^{\text{eff}}(z) = \tilde{C}_{L}(z)\delta_{RR'}\delta_{LL'} + \tilde{\Delta}_{L}^{1/2}(z)\{S^{0}[1-\tilde{\gamma}(z)S^{0}]^{-1}\}_{RL,R',L'}\tilde{\Delta}_{L'}^{1/2}(z) .$$
⁽²⁷⁾

The energy-dependent translationally invariant effective Hamiltonian $H^{\text{eff}}(z)$ represents just the intuitively expected result of the application of the CPA to the Hamiltonian (12): the random-potential parameters C_L , Δ_L , and γ_L are substituted by their coherent-potential counterparts: $\tilde{C}_L(z)$, the effective atomic levels; $\tilde{\Delta}_L(z)$, the effective band widths; and $\tilde{\gamma}_L(z)$, the effective band distortions. On the other hand, the common TB-CPA theories are able to treat correctly only the diagonal disorder (different atomic levels). The off-diagonal disorder (different bandwidths and band shapes) can be treated within these theories only if one adopts further approxi-

IV. PHYSICAL QUANTITIES

errors.

mations which, however, may introduce uncontrollable

In this section we will apply the expression for the configurationally averaged GF, Eqs. (22) or (24), to evalu-

ate some physically relevant quantities related to random alloys.

A. The charge density and the density of states

These are the simplest quantities obtained from the on-site elements of the averaged GF. The projected charge density related to the orbital symmetry L and to the atom Q = A, B is

$$\rho_L^Q(E,r) = [\varphi_L^Q(E,r)]^2 \varphi_L^Q(E) , \qquad (28)$$

where $\varphi_L^Q(E, r) = \varphi_L^Q(E, |r|) Y_L(\hat{\mathbf{r}})$ is the normalized solution of radial scalar-relativistic Schrödinger equations in the sphere occupied by atom Q, and $\varphi_L^Q(E)$ is the projected local density of states (DOS):

$$\mathcal{G}_{L}^{Q}(E) = -\frac{\dot{P}_{L}^{\beta,Q}(E)}{\pi} \operatorname{Im} \Phi_{L}^{\beta,Q}(E+i0) ,$$

$$\Phi_{L}^{\beta,Q}(z) = \frac{1}{c^{Q}} \langle g^{\beta}(z) \rangle_{RL,RL}^{QQ} .$$
(29)

The total projected DOS is given by

$$\begin{split} \Phi_{L}^{\beta,A}(z) &= \frac{1}{c^{A}} \left[\frac{[P_{L}^{\beta,B}(z) - \mathcal{P}_{L}^{\beta}(z)]^{2} \Phi_{L}^{\beta}(z) - [\mathcal{P}_{L}^{\beta}(z) - \langle P_{L}^{\beta}(z) \rangle]}{[\Delta P_{L}^{\beta}(z)]^{2}} \right] \\ &= -\frac{P_{L}^{\beta,B}(z) - \mathcal{P}_{L}^{\beta}(z)}{c^{A} \Delta P_{L}^{\beta}(z)} \Phi_{L}^{\beta}(z) = \frac{\Phi_{L}^{\beta}(z)}{1 + [P_{L}^{\beta,A}(z) - \mathcal{P}_{L}^{\beta}(z)] \Phi_{L}^{\beta}(z)} \end{split}$$

if we employ the CPA equation (19). Using the definition of $\Omega_L^\beta(z)$, Eq. (19''), we obtain finally

$$\varphi_{L}^{Q}(E) = -\frac{\dot{P}_{L}^{\beta,Q}(E)}{\pi} \operatorname{Im}[P_{L}^{\beta,Q}(E) - \Omega_{L}^{\beta}(E+i0)]^{-1}.$$
 (31)

This surprisingly simple expression allows us also to understand the physical meaning of the coherent interactor $\Omega_L^\beta(z)$ introduced in (19"). It describes the effective energy-dependent coupling of a given site R to all other sites in a random alloy.

The total DOS is

$$\varphi(E) = \sum_{L} \varphi_{L}(E) = \sum_{Q} \sum_{L} c^{Q} \varphi_{L}^{Q}(E) , \qquad (32)$$

and, in terms of it, the Fermi energy E_F of a random alloy is

$$\int_{-\infty}^{E_F} \mathscr{G}(E) dE = \sum_{Q} c^{Q} Z^{Q} , \qquad (33)$$

where Z^{Q} is the number of valence electrons corresponding to the alloy component Q.

The electron density $n^{Q}(r)$, r = |r|, spherically averaged in its own sphere and corresponding to an atom Q is

$$n^{Q}(\boldsymbol{\kappa}) = \frac{1}{4\pi} \sum_{L} \int_{-\infty}^{E_{F}} \rho_{L}^{Q}(E,\boldsymbol{\kappa}) dE$$
$$= \frac{1}{4\pi} \sum_{L} \int_{-\infty}^{E_{F}} [\varphi_{L}^{Q}(E,\boldsymbol{\kappa})]^{2} \varphi_{L}^{Q}(E) dE \quad . \tag{34}$$

$$\mathcal{G}_{L}(E) = -\frac{1}{\pi} \operatorname{Im} \langle G(E+i0) \rangle_{RL,RL} ,$$

$$\langle G(z) \rangle_{RL,RL} = \sum_{Q} c^{Q} \dot{P}_{L}^{\beta,Q}(z) \Phi_{L}^{\beta,Q}(z) .$$
(30)

In writing (29) and (30), we have employed (15) and the fact that $\lambda_L^{\beta}(E)$ is the real function. It holds, e.g., for Q = A,

In order to perform the charge self-consistent alloy calculations in the ASA within the density-functional formalism,^{2,13} one merely needs the electron densities $n^{Q}(\kappa)$. One remark is now in order: the functions $\dot{P}_{L}^{\beta,Q}(E)$ have poles at energies $\varepsilon_{L}^{Q} = C_{L}^{Q} - \Delta_{L}^{Q} / (\gamma_{L}^{Q} - \beta_{L})$. If $E = \varepsilon_{L}^{Q}$, the expression (29) is singular and it will contribute by spurious δ functions to the local DOS. These contributions are canceled by the site-diagonal term $\lambda_{L}^{\beta,Q}(E)$, Eq. (14), which was neglected when we derived Eq. (29) because, in practice, these poles usually lie above the occupied states for standard choice^{2,12} of $E_{\nu L}$ in the middle of the occupied energy states.

B. The integrated density of states

This quantity, which gives the number of states up to an energy E, is defined as

$$N(E) = -\frac{1}{\pi N} \operatorname{Im} \sum_{R,L} \int_{-\infty}^{E} \langle G(\xi + i0) \rangle_{RL,RL} d\xi$$
$$\equiv -\frac{1}{\pi N} \operatorname{Im} \operatorname{Tr} \int_{-\infty}^{E} \langle G(\xi + i0) \rangle d\xi . \qquad (35)$$

The CPA expression for N(E) for a single-band TB model has been given by Ducastelle,¹⁴ while its matrix generalization was given in Ref. 15. Here, we generalize it for energy-dependent potentials $P_L^{\beta,Q}(z)$, which appear in our CPA theory. It holds (the overdot denotes the energy derivative, and we omit the energy argument to simplify the writing):

$$\frac{d}{dz} \sum_{L} \sum_{Q} c^{Q} \ln[1 + (P_{L}^{\beta,Q} - \mathcal{P}_{L}^{\beta})\Phi_{L}^{\beta}] = \sum_{L} \sum_{Q} c^{Q} \{ [1 + (P_{L}^{\beta,Q} - \mathcal{P}_{L}^{\beta})\Phi_{L}^{\beta}]^{-1} [(P_{L}^{\beta,Q} - \mathcal{P}_{L}^{\beta})\dot{\Phi}_{L}^{\beta} + (\dot{P}_{L}^{\beta,Q} - \dot{\mathcal{P}}_{L}^{\beta})\Phi_{L}^{\beta}] \}$$
$$= \sum_{L} \sum_{Q} c^{Q} \Phi_{L}^{\beta,Q} (\dot{P}_{L}^{\beta,Q} - \dot{\mathcal{P}}_{L}^{\beta}) = \sum_{L} [\langle G \rangle_{LL}] - \sum_{L} \dot{\mathcal{P}}_{L}^{\beta} \Phi_{L}^{\beta} .$$

The third form follows after invoking Eq. (19) and the last form after using (30) and (19''). Employing (20), we verify the identity

$$\frac{d}{dz}\frac{1}{N}\sum_{k}\operatorname{Tr}\ln[\mathcal{P}^{\beta}(z)-S^{\beta}(k)] = \frac{d}{dz}\sum_{k}\ln\det\|\mathcal{P}^{\beta}_{L}(z)\delta_{LL'}-S^{\beta}_{LL'}(k)\|$$
$$=\frac{1}{N}\sum_{k}\operatorname{Tr}[\mathcal{P}^{\beta}(z)-S^{\beta}(k)]^{-1}\dot{\mathcal{P}}^{\beta}(z)=\sum_{L}\dot{\mathcal{P}}^{\beta}_{L}(z)\Phi^{\beta}_{L}(z).$$

Using this, we obtain finally

$$N(E) = -\frac{1}{\pi N} \operatorname{Im} \sum_{k} \sum_{L} \ln \det \|\mathcal{P}_{L}^{\beta}(z)\delta_{LL'} - S_{LL'}^{\beta}(k)\|_{E+i0} - \frac{1}{\pi} \operatorname{Im} \sum_{L} \sum_{Q} c^{Q} \ln \{1 + [P_{L}^{\beta,Q}(z) - \mathcal{P}_{L}^{\beta}(z)]\Phi_{L}^{\beta}(z)\}_{E+i0} .$$
(36)

The integrated DOS enters the formula for the configurationally averaged ground-state energy of random alloys.¹⁶

C. The Bloch spectral density and the self-energy

The notion of energy bands ceases to exist in random alloys due to the loss of the translational symmetry. It is substituted by the notion of Bloch spectral density A(k,E). For a perfect solid, A(k,E) is simply a sum of Dirac δ functions located at the band energies $E_v(k)$,

$$A(k,E) = \sum_{v} \delta(E - E_{v}(k)) . \qquad (37)$$

In random alloys

$$A(k,E) = -\frac{1}{\pi} \operatorname{Im} \sum_{L} \left\langle G(k,E+i0) \right\rangle_{LL} , \qquad (38)$$

which can be evaluated straightforwardly using (24). The Bloch spectral density (38), when compared to its crystal counterpart (37), gives a valuable information concerning the shift and broadening of crystal bands $E_v(k)$ on alloying. Such information, and even more detailed information, can be obtained from the self-energy operator $\Sigma(z)$ defined in the following manner:

$$\langle G(z) \rangle = [z \parallel -H^{\text{ref}} - \Sigma(z)]^{-1} .$$
(39)

Here, H^{ref} is the reference Hamiltonian with respect to which $\Sigma(z)$ is defined, e.g., the virtual-crystal average of (12). The self-energy $\Sigma(z)$ is obtained from (39) as

$$\Sigma_{RL,R'L'}(z) = z \,\delta_{RR'}\delta_{LL'} - H_{RL,R'L'}^{\text{ref}} - \{\langle G(x) \rangle\}_{RL,R'L'}^{-1} .$$
(40)

It is expressed via the inverse of the configurationally averaged GF matrix. Such an inverse can be found in a closed form for the GF, (22), as we have demonstrated recently.¹⁷ The result is

$$[\langle G(z) \rangle]_{RL,R'L'}^{-1} = [\Lambda_L^{\beta}(z)]^{-1} \delta_{RR'} \delta_{LL'} - N_L^{\beta}(z) \langle \tilde{g}^{\beta}(z) \rangle_{RL,R'L'} N_{L'}^{\beta}(z) ,$$

$$N_L^{\beta}(z) = [\Lambda_L^{\beta}(z)]^{-1} M_L^{\beta}(z) , \qquad (41)$$

$$\langle \tilde{g}^{\beta}(z) \rangle_{RL,R'L'} = \{ [\tilde{\mathcal{P}}^{\beta}(z) - S^{\beta}]^{-1} \}_{RL,R'L'} ,$$

$$\tilde{\mathcal{P}}_L^{\beta}(z) = \mathcal{P}_L^{\beta}(z) + [M_L^{\beta}(z)]^2 [\Lambda_L^{\beta}(z)]^{-1} .$$

There is thus a striking formal similarity between $\langle G(z) \rangle$ and its inverse. The expression for $\sum_{RL,R'L'}(z)$ in the site representation is obtained from (40) and (41), while the Bloch transform of (40) gives $\sum_{LL'}(k,z)$ in the wavevector representation. The self-energy is, generally, nondiagonal with respect to orbital indices *L* and *L'*, even for cubic lattices, in contrast with the coherent-potential function $\mathcal{P}_{L}^{\beta}(z)$. The self-energy is naturally *k* dependent as the Hamiltonian (12) exhibits the off-diagonal randomness. Alternatively, in the site representation, the selfenergy is not the single-site quantity, but it couples a given site R to its few nearest neighbors. This should be contrasted with common TB-CPA theories, where $\Sigma(z)$ is the site-diagonal or k-independent quantity. The knowledge of $\Sigma_{LL'}(k,z)$ allows us to understand the finest details of the influence of disorder on the electronic structure, as shown in Ref. 17, to which we refer the reader for further details.

V. APPROXIMATE TREATMENT OF CHARGE SELF-CONSISTENCY AND LATTICE-RELAXATIONS EFFECTS

Inputs of our theory are the lattice structure and the potential parameters C_L^Q , Δ_L^Q , and γ_L^Q of species Q = A, B forming a disordered alloy $A_x B_{1-x}$. We have demonstrated in the last section that our theory allows us to construct the spherical charge density $n^Q(\varkappa)$, which is all we need to perform the charge self-consistent calculations for random alloys within the ASA. The necessary formulas are given in Ref. 13. We only need to substitute the MT spheres by the corresponding WS spheres and neglect the contributions from the interstitial space.

The flexibility in the choice of the ASA radii allows us to include the effects of charge self-consistency and lattice relaxations approximately, yet accurate without the need for full self-consistency. Our method represents an adaptation of the method proposed by Andersen² for the case of ordered binary alloys to the case of random alloys.

The starting points are the potential parameters and their volume derivatives¹² for elementary metals. The idea is to choose the atomic-sphere radii of alloy species in such a way that spheres are approximately charge neutral. The constraints are that spheres fill in all space and that the validity of the ASA, Eq. (10), is preserved. The simplest choice is to use generally different equilibrium WS radii of pure species. As we shall see later, this is the proper choice when Vegard's law is satisfied. The generalization to the case, when Vegard's law is not satisfied, which is the case if the binding in the alloy is different from that in pure crystals, is also possible. If V^Q and V_Q^0 (Q = A, B) are the actual and equilibrium WS-sphere volumes, the preservation of the alloy volume V^{alloy} requires

$$xV^{A} + (1-x)V^{B} = V^{\text{alloy}}$$
(42a)

Assuming the linear pressure-volume relations with bulk moduli B_0^Q for the elements, we have²

$$(V^{A} - V_{0}^{A}) / V_{0}^{A} : (V^{B} - V_{0}^{B}) / V_{0}^{B} = B_{0}^{B} : B_{0}^{A}$$
. (42b)

The solution of Eqs. (42) is

$$V^{A} = \frac{B_{0}^{B} V^{\text{alloy}} + (1-x) V_{0}^{B} (B_{0}^{A} - B_{0}^{B})}{x V_{0}^{A} B_{0}^{B} + (1-x) V_{0}^{B} B_{0}^{A}} V_{0}^{A} ,$$

$$V^{B} = \frac{B_{0}^{A} V^{\text{alloy}} - x V_{0}^{A} (B_{0}^{A} - B_{0}^{B})}{x V_{0}^{A} B_{0}^{B} + (1-x) V_{0}^{B} B_{0}^{A}} V_{0}^{B} .$$
(43)

If Vegard's law is satisfied, $V^{\text{alloy}} = xV_0^A + (1-x)V_0^B$, the solution is trivial, $V^Q = V_0^Q$ (Q = A, B), as mentioned above. New ASA radii $s^Q = (3V^Q/4\pi)^{1/3}$, and equilibrium radii $s_0^Q = (3V_0^Q/4\pi)^{1/3}$ are used to determine new potential parameters as²

$$C_{L}^{Q} = C_{0L}^{Q} + \frac{dC_{L}^{Q}}{d \ln s^{Q}} \ln \left[\frac{s^{Q}}{s_{0}^{Q}} \right],$$

$$\gamma_{L}^{Q} = \gamma_{0L}^{Q} + \frac{d\gamma_{L}^{Q}}{d \ln s^{Q}} \ln \left[\frac{s^{Q}}{s_{0}^{Q}} \right],$$

$$\Delta_{L}^{Q} = \Delta_{0L}^{Q} \left[\frac{s^{Q}}{s_{0}^{Q}} \right]^{d \ln \Delta_{L}^{Q}/d \ln s^{Q}}.$$
(44)

Here, the subscript 0 denotes equilibrium quantities. The volume derivatives $dC_L^Q/d \ln s^Q$, $d\gamma_L^Q/d \ln s^Q$, and $d \ln \Delta_L^Q/d \ln s^Q$ are obtained from the self-consistent LMTO-ASA calculations at different sphere radii, and their values for $s^Q = s_Q^0$ are used in the definition of the potential parameters.^{2,10} Thus, after extrapolation of potential parameters to new radii, we must take into account that the WS radius of the alloy, $w^{\text{alloy}} = (3V^{\text{alloy}}/4\pi)^{1/3}$, is different from s^Q 's. To correct this, we should multiply Δ_L^Q and γ_L^Q by $(s^Q/w^{\text{alloy}})^{2l+1}$, and leave C_L^Q unchanged.² The different sizes of atoms cause some structural deformations in random alloys, so that the structure constant $S_{RL,R'L'}^Q$ is slightly changed and dependent on the occupation of sites R and R' by atoms Q and Q', respectively. Such deformations are missing in ordered binary alloys. To account for them approximately, we set

$$S_{RL,R'L'}^{o,QQ'} \approx S_{RL,R'L'}^{0} [w^{\text{alloy}} / (s^{Q_{S}Q})^{1/2}]^{l+l'+1} , \qquad (45)$$

where $S_{RL,R'L'}^0$ is the structure constant of a perfect, unrelaxed lattice. In deriving (45), we have assumed the dependence of $S_{RL,R'L'}^0$ on the relative change of distance $d^{QQ'} = |R - R'|$ between the sites R and R' occupied by atoms Q and Q', in the form $d^{QQ'} \approx d_0[(s^Q + s^{Q'})/2w^{\text{alloy}}]$. Here d_0 is the corresponding average distance between the points R and R' in an unrelaxed lattice with the averaged WS radius w^{alloy} . For values of s^Q typical for transition metals, the quantity $(s^Q + s^{Q'})/2w^{\text{alloy}}$ is close to $(s^Q s^{Q'})^{1/2}/w^{\text{alloy}}$, from which follows Eq. (45). Also, we assume that (45) holds locally; this means that it is not influenced by the occupation of sites other than R and R'. The alloy Hamiltonian now becomes

$$H_{RL,R'L'}^{\gamma,QQ'} = C_L^Q \delta_{RR'} \delta_{LL'} \delta_{QQ'} + (\Delta_L^Q)^{1/2} S_{RL,R'L'}^{\gamma,QQ'} (\Delta_{L'}^{Q'})^{1/2} ,$$

$$S_{RL,R'L'}^{\gamma,QQ'} = \{ S^0 + S^0 \gamma S^0 + \cdots \}_{RL,R'L'}^{QQ'} .$$
(46)

It can be verified that factors $[(s^{Q_sQ'})^{1/2}/w^{\text{alloy}}]^{l+l'+1}$ coming from $(\Delta_L^Q)^{1/2}(\Delta_{L'}^{Q'})^{1/2}$, and $[w^{\text{alloy}}/(s^{Q_{S}Q'})^{1/2}]^{l+l'+1}$, coming from $S^{0,QQ'}_{RL,R'L'}$, cancel each other. We thus arrive at a surprisingly simple result: we can use the unrelaxed structure constant $S^{0}_{RL,R'L'}$ and the potential parameters as given by (44). If Vegard's law is valid, the alloy parameters are equal to the parameters of pure crystals evaluated at their equilibrium lattice constants. Note, however, that this simple result is a consequence of a rather sophisticated interplay between the charge self-consistency and lattice relaxations due to different sizes of atoms forming the random alloy. We have essentially employed the fact that the radii of WS spheres of atomic species can be different within the ASA.

On the contrary, in the KKR-CPA one chooses the common radii r^{alloy} of touching MT spheres, $r^{\text{alloy}} = xr^A + (1-x)r^B$, in a random binary alloy $A_x B_{1-x}$, where r^A and r^B are MT radii of atoms A and B. The interstitial space, which is about one-third of the alloy volume for close-packed lattices, is thus excluded from self-consistency. The use of common radii even for atoms with very different sizes (e.g., for Cu and Pd) thus introduces artificially some sort of the charge transfer, which must be treated self-consistently. The greater Pd atom then becomes overscreened within a small MT with the radius r^{alloy} , especially for a low concentration of Pd atoms, when $r^{\text{alloy}} \approx r^{\text{Cu}} < r^{\text{Pd}}$. This overscreening is due to a limited space where the self-consistency is performed. The impurity Pd potential becomes more attractive and shifts the d states of Pd downwards.¹⁸ This inconsistency can be relaxed either by a proper treatment of the charge transfer outside the impurity MT sphere by performing self-consistent calculations for a cluster consisting of a central Pd sphere surrounded by Cu spheres, or, by enlarging the radius of Pd spheres as in our case. The results are similar in both cases,^{9,19} as well as the ability to include approximately the effect of lattice relaxations. The main advantage of our approach in comparison with that adopted in Ref. 18 is that it can be generalized also to the case of concentrated random alloys.

The experience with ordered binary alloys² as well as with numerous applications to random binary al $loys^{4,20-23}$ using the method outlined above confirms its accuracy. The success of our approximate treatment is due to the fact that the internal energy zeroes of the nearly neutral ASA spheres line up, which should be contrasted with the mismatch of the MT zeros of constituents in the KKR-CPA method. This allows us to relate the potential functions of constituents on the energy scale with respect to a common energy zero without performing self-consistent calculations. Also the trimodal (A-A, A-B, and B-B) distribution of interatomic distances, which is a consequence of our choice of different sizes of ASA spheres, is consistent with experiment.²⁴ Our approximate method thus gives a simple, yet consistent and accurate, treatment of the combined effect of charge selfconsistency and lattice relaxations in random transitionmetal alloys.

VI. COMPUTATIONAL ASPECTS

In this section we present the results of numerical studies on a number of transition-metal alloys, using approximate treatment of the charge self-consistency and lattice relaxations described in the previous section.

A. Computational details

The screened fcc and bcc structure constants $S_{LL'}^{\beta}(k)$, which enter the CPA equations, have been obtained by a Bloch transform from the tabulated values of the realspace screened structure constant.¹² Only the first, and the first- and second-nearest neighbors of $S_{RL,R'L'}^{\beta}$ are needed for accurate band structures of fcc and bcc transition metals, respectively (see Figs. 1 and 2). The k integration necessary to evaluate $\Phi_L^\beta(z)$ [Eq. (20)] has been performed for a regular network of k points in the irreducible wedge of the Brillouin zone (BZ). Division of the $\Gamma - X$ edge into 14 equal parts for the fcc lattice, and the $\Gamma - H$ edge into 16 parts for the bcc lattice, representing approximately 250 k points in the irreducible BZ in both cases, has been used. However, the calculations using approximately 100 k points [the $\Gamma - X$ ($\Gamma - H$) edges divided into 10 (12) equal parts] yielded essentially the same results. The integration method employed takes advantage of using energy variables with finite imaginary parts, thereby smoothing out the integrand and speeding up the iteration process. The desired quantities are found by the numerical analytical continuation back to the real axis²⁵ in the last step of the numerical calculations. The step in energy and its imaginary part were chosen to be 0.01 Ry. The CPA equations (19) or (19") converged in every case. In practical calculations, Eqs. (19'') for unknown $\Omega^{\beta}_{\mu}(z)$, $\mu = s$, p, t_{2g} , and e_g , have been preferred. Below, we present results of the full CPA solution, but nearly the same results^{4,21} are obtained for a simplified case, when only $\Omega^{\beta}_{t_{2e}}$ and $\Omega^{\beta}_{e_{e}}$ are calculated from the corresponding CPÅ equations, but the approximation $\Omega^{\beta}_{\mu}(z) = x \Omega^{\beta,A}_{\mu}(z) + (1-x) \Omega^{\beta,B}_{\mu}(z)$ is employed for $\mu = s$ and p. Here, $\Omega_{\mu}^{\beta,Q}(z)$, Q = A or B, are given by (19") with $\mathcal{P}_{\mu}^{\beta}(z)$ substituted by its "virtual-crystal" value $xP_{\mu}^{\beta,A}(z) + (1-x)P_{\mu}^{\beta,B}(z)$. The simplicity of computer codes makes it possible to run the CPA program easily even on personal computers.

B. Band structures

In Figs. 1 and 2, we present the band structures of two typical transition metals, namely fcc copper and paramagnetic bcc iron, to give the reader a feeling of the accuracy of the TB-LMTO method. The bands were obtained from the solution of the eigenvalue equation (9a) in the orthogonal MTO representation γ . The valence bands and the conduction bands not very far from the Fermi energy agree nicely with the textbook ones.²⁶ They were obtained using the tabulated values of potential parameters for equilibrium lattice constants.¹² The corresponding densities of states are given in Figs. 5 and 7, and they also agree well with the standard ones.²⁶

C. Specific alloy systems

Here we present the result of calculations for total and component densities of states of random substitutional



FIG. 1. The band structure of fcc copper along the $\Gamma - X - W - L - \Gamma$ line in the Brillouin zone. The horizontal line indicates the position of the Fermi level E_F .

transition-metal alloys $Ag_x Pd_{1-x}$, $Cu_x Pd_{1-x}$, and $Ti_x Fe_{1-x}$, as well as of the Bloch spectral densities for selected alloy concentrations. The reasons for this choice are the following. (i) The (Ag,Pd) system represents an alloy with dominating diagonal or level disorder, weak off-diagonal disorder, and small mismatch in atomic sizes of constituents, as they come from the same row of the Periodic Table. (ii) The (Cu,Pd) system is a typical nonisocoric alloy of elements belonging to different columns of the Periodic Table; in this system the off-diagonal disorder and the charge self-consistency play an important role.²⁷ In addition, there is a sizable difference in lattice constants of pure constituents. (iii) The (Ti,Fe) system is



FIG. 2. The band structure of paramagnetic bcc iron along the $\Gamma - H - N - P - \Gamma$ line in the Brillouin zone. The horizontal line indicates the position of the Fermi level E_F .

a bcc random alloy with very different sizes of atomic constituents and strong diagonal disorder, exhibiting a pronounced tendency to form an ordered CsCl structure for the $Ti_{50}Fe_{50}$ composition. (iv) For all systems studied, the theoretical results based on the self-consistent-field (SCF) KKR-CPA method as well as a number of experimental results are available, thus making a direct comparison possible.

1. fcc $Ag_x Pd_{1-x}$ random alloy

The results for this alloy are presented in Figs. 3 and 4 for the total, Eq. (32), as well as for the Ag and Pd component densities of states, Eq. (31), and for the Bloch spectral densities (38), respectively. For the Ag-rich alloy there is a clearly pronounced impurity peak due to Pd atoms, which reflects itself also in a highly nonLorentzian behavior of the spectral density peaks. Note that the disorder-induced part of the spectra does not move with the change on the k vector, contrary to weakly damped *s*-band peaks below and above the region of *d* states. This justifies the approximate solution of the CPA equations for the *s* and *p* states mentioned in Sec. VI A and adopted in previous papers, Refs. 4 and 20, where also coarse mesh of k points in the irreducible wedge of the Brillouin zone was used. The comparison shows no significant de-



FIG. 3. The total (solid line) and the local (not concentration-weighted) densities of states on Ag (long-dashed line) and on Pd (short-dashed line) atoms in fcc $Ag_x Pd_{1-x}$ random alloys. The concentrations x are assigned to corresponding curves. The vertical lines indicates the position of the Fermi level.



FIG. 4. The spectral densities for fcc $Ag_{75}Pd_{25}$ random alloys. The points in the Brillouin zone are as follows: point X, $\mathbf{k} = (1,0,0)$ (top line); $\mathbf{k} = (\frac{1}{2},0,0)$; point Γ , $\mathbf{k} = (0,0,0)$; $\mathbf{k} = (\frac{1}{4},\frac{1}{4},\frac{1}{4})$; and point L, $\mathbf{k} = (\frac{1}{2},\frac{1}{2},\frac{1}{2})$ (bottom line). The short vertical lines indicate the position of the Fermi level.

viations from the present full CPA treatment. We note overall quantitative agreement of our results with the SCF KKR-CPA results of Ref. 28. On the other hand, the non-self-consistent KKR-CPA method²⁹ overestimates the splitting of the Ag- and Pd-related d resonances and it gives quantitatively incorrect results, as discussed in Ref. 28. The corresponding empirical TB-CPA results³⁰ agree reasonably with our results and those of Ref. 28 because the dominating level disorder is properly described, and the shapes of the densities of states of constituents are similar and the relative position of the Ag and Pd bands on the energy scale determined³⁰ by aligning crystal Fermi levels works well in this particular case.

2. fcc $Cu_x Pd_{1-x}$ random alloy

The results for this alloy are presented in Figs. 5 and 6 in a form similar to that for the (Ag,Pd) system. Contrary to the previous case we observe a common-band behavior for all alloy concentrations. The overall effects of disorder, which is predominantly an off-diagonal one, is weaker than in the (Ag,Pd) system. This can be clearly seen on spectral densities. Let us note that the effect of disorder is stronger at the BZ boundaries than in the BZ center. Overall agreement of our results with those of the SCF KKR-CPA ones²⁷ is again very good, but there are still some important differences to be noted. Our Pd density of states for a Cu₇₅Pd₂₅ alloy is narrower by about 0.75 eV, and the low-energy peak approximately at -0.5



FIG. 5. The same as in Fig. 3, but for fcc $Cu_x Pd_{1-x}$ random alloys. The local densities of states on Cu and Pd atoms are given by long- and short-dashed lines, respectively.

Ry is much less intensive and its center of gravity is shifted upwards. This is in accordance both with experiment³¹ and the sophisticated single-impurity calculations of Ref. 18, and the reason for this was discussed in Sec. V. On the other hand, the agreement of the empirical TB-CPA approach³⁰ in this case is much worse than for the (Ag,Pd) alloy. It particularly concerns the details of the densities of states and spectral densities. This is due to the inability of the empirical TB-CPA method to treat properly the off-diagonal disorder and to determine the relative positions of the alloy constituents on the energy scale without empirical adjustment. It is important to note that also the non-self-consistent KKR-CPA method³² fails to give correct results without empirical adjustment of the relative positions of the *d*-phase shifts of Cu and Pd. No such adjustment is needed in our approach, as was discussed in Sec. V.

3. bcc $Ti_x Fe_{1-x}$ random alloy

The results for this alloy are presented in Figs. 7 and 8 in the form similar to previous cases. This alloy exhibits strong diagonal disorder, non-negligible off-diagonal disorder, and the constituent atoms have very different sizes. This indicates a necessity for, at least an approximate, treatment of the lattice-relaxation effects, as explained in Sec. V. The bcc disordered phase exists for Ti-rich alloys $(x \ge 0.77)$, and for x = 0.5 the ordered CsCl phase is known to exist and to be very stable. We have calculated





FIG. 6. The same as Fig. 6, but for fcc $Cu_{75}Pd_{25}$ random alloys.

FIG. 7. The same as in Fig. 3, but for bcc $Ti_x Fe_{1-x}$ random alloys. The local densities of states on Ti and Fe atoms are given by short- and long-dashed lines, respectively.

also the density of states and the spectral densities for the hypothetical disordered bcc phase of Ti₅₀Fe₅₀. A similar study was done in Ref. 33, where comparison of the SCF KKR-CPA results for the disordered bcc phase of Ti₅₀Fe₅₀ with the self-consistent LMTO results for its ordered CsCl phase was made. Such comparisons allows us to explain the order-disorder phenomena in the alloy system and the stability of the ordered phase. This point was discussed in detail in Ref. 33 and it need not be repeated here. Instead, we compare our densities of states and the spectral densities for disordered bcc-based Ti₅₀Fe₅₀ alloy with the results of SCF KKR-CPA calculations.³³ We have assumed the lattice constant of the disordered phase according to Vegard's law, which is about 3% greater than the lattice constant of the ordered CsCl phase. It seems to be a reasonable choice due to the disorder and the size mismatch of Ti and Fe atoms. We note again very good overall agreement with the results of Ref. 33, especially concerning the disappearance of the pseudogap at E_F present in the ordered phase. The fact that the minima and maxima in the Ti and Fe densities of states do not follow each other and the non-Lorentzian behavior of the spectral densities, clearly show, again in agreement with Ref. 33, that the strong disorder is present in this alloy. On the other hand, our Ti density of states (larger atom) has a center of gravity shifted up-



FIG. 8. The spectral densities for bcc $Ti_{50}Fe_{50}$ random alloys. The points in the Brillouin zone are as follows: point *P*, $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (top line); $\mathbf{k} = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$; point Γ , $\mathbf{k} = (0,0,0)$; $\mathbf{k} = (\frac{1}{2}, 0, 0)$; and point *H*, $\mathbf{k} = (1,0,0)$ (bottom line). The short vertical lines indicate the position of the Fermi level alloy.

wards, and the local maximum at ≈ -0.3 Ry is missing in our calculations in comparison with the SCF KKR-CPA ones. This situation is quite similar to that found for Pd atoms in the Cu₇₅Pd₂₅ alloy, and it is thus reasonable to assume that it has the same origin (see Sec. V). We have found a similar effect also in the Au density of states in Cu₇₅Au₂₅ random alloys, and the detailed analysis of this interesting phenomenon and its consequences for the experimental results will be discussed in a separate paper.

The results presented in this section demonstrate the ability of the present approach to describe the electronic structure of random transition-metal alloys with accuracy comparable to that of the SCF KKR-CPA method. Its first-principles character and the possibility to treat approximately, yet consistently, the charge selfconsistency and lattice-relaxation effects are important advantages in comparison with other TB-CPA approaches.

VII. DISCUSSION AND CONCLUSIONS

In the last few years the KKR-CPA method, particularly its charge self-consistent version,¹² supplanted calculationally and interpretationally simpler TB-CPA approaches. Main objections against the TB-CPA method had been summarized as follows. (i) It is a semiempirical, rather than a first-principles theory which suffers from ambiguities in determination of the Slater-Koster parameters of the alloy. (ii) It is inadequate to treat the offdiagonal randomness which frequently occurs in transition-metal alloys. (iii) The charge self-consistent solution is impossible due to the lack of reliable wave functions.

Recently, there were some attempts to weaken at least some of the above limitations of the TB-CPA theories. The highly accurate Slater-Koster fits to first-principles band structures of constituents, superior to earlier sets of TB parameters, were used in the TB-CPA method of Ref. 30. However, only the diagonal randomness is included properly, while the off-diagonal disorder is treated approximately, within the virtual-crystal approximation. Also, the element $H_{RL,R'L'}^{AB}$ of the alloy Hamiltonian be-tween the sites $R \neq R'$ occupied by inequal atoms is uncertain and it has to be guessed in some way. The effect of off-diagonal disorder in the d states was included properly within the universal TB parametrization scheme of Harrison, employing the multiplicative nature of hopping integrals.³⁴ However, the quality of the description of band structures of transition metals is not sufficient in this scheme³⁵ when compared to the KKR or LMTO methods and the approach still remains an empirical one. The first-principles LCAO-CPA method, based on the density-functional approach, has been developed recently.¹⁴ This method provides, in addition, a reliable wave function that can be used eventually for the charge selfconsistent alloy calculations. The formal difference from the current TB-CPA methods, like that of Ref. 30, consists of the explicit appearance of the overlap matrix in the CPA equations. A special linear combination of atomic orbitals (LCAO) basis, optimally localized in space, allows us to reduce the off-site disorder in the Hamiltonian and overlap matrices to some extent, but it still must be treated approximately as in Ref. 30.

The above approaches can be now contrasted with our new TB LMTO-CPA method, which preserves the computational and interpretational simplicity of the empirical TB-CPA schemes, but offers, in addition, the following novel and attractive features: (i) It is a first-principles method, based on the density-functional formalism and it describes the electronic structure of metals with accuracy comparable to that obtained from other first-principles approaches. (ii) It treats the diagonal as well as offdiagonal and hybridizational disorders on equal footing within the CPA just as the KKR-CPA method does. (iii) It provides the explicit expression for the element $H_{RL,R'L'}^{AB}$ of the alloy Hamiltonian. (iv) It allows for an approximate, yet accurate treatment of combined effects of the charge self-consistency and lattice relaxations. (v) It provides the reliable wave functions, the TB-LMTO's, which can be used, e.g., for the charge self-consistent calculations or the evaluation of the optical transitionmatrix elements needed for the calculation of the dielectric function $\epsilon_2(\omega)$ or the photoemission spectra. (vi) The simplicity of the TB LMTO-CPA scheme allows a straightforward application to various physical effects related to random transition-metal alloys, including the transport properties and surface phenomena.³⁷

APPENDIX

We shall derive the expressions for $\langle g^{\beta}(z) \rangle_{RL,R'L'}^{QQ'} = \langle \eta_R^Q g_{RL,R'L'}^{\beta}(z) \eta_R^{Q'} \rangle$. From the definitions

$$P_{RL}^{\beta}(z) = \sum_{Q} \eta_R^Q P_L^{\beta,Q}(z), \quad \sum_{Q} \eta_R^Q = 1 \quad , \tag{A1}$$

we obtain

$$\eta_R^A = -\frac{P_L^{\beta,B}(z) - P_{RL}^{\beta}(z)}{\Delta P_L^{\beta}(z)} ,$$

$$\eta_R^\beta = \frac{P_L^{\beta,A}(z) - P_{RL}^{\beta}(z)}{\Delta P_L^{\beta}(z)} ,$$
(A2)

where $\Delta P_L^{\beta}(z) = P_L^{\beta, A}(z) - P_L^{\beta, B}(z)$. The next step is to eliminate the random quantity $P_{RL}^{\beta}(z)$, employing the definition of $g^{\beta}(z)$ [Eq. (14)] and $\langle g^{\beta}(z) \rangle$ [Eq. (18)]. We obtain, in the matrix form,

$$P^{\beta}(z) = \mathcal{P}^{\beta}(z) + [g^{\beta}(z)]^{-1} - [\langle g^{\beta}(z) \rangle]^{-1} .$$
 (A3)

Let us evaluate, e.g., the quantity $\langle g^{\beta}(z) \rangle_{RL,R'L'}^{AA}$. Using (A2), we have

$$\langle g^{\beta}(z) \rangle_{RL,R'L'}^{AA} = \langle [P_L^{\beta,B}(z) - P_{RL}^{\beta}(z)]g_{RL,R'L'}^{\beta}(z) \\ \times [P_L^{\beta,B}(z) - P_{RL}^{\beta}(z)] \rangle \\ \times [\Delta P_L^{\beta}(z)\Delta P_{L'}^{\beta}(z)]^{-1} .$$
 (A4)

We shall further employ the matrix identities

$$\langle P^{\beta}(z)g^{\beta}(z) \rangle = \mathcal{P}^{\beta}(z) \langle g^{\beta}(z) \rangle ,$$

$$\langle g^{\beta}(z)P^{\beta}(z) \rangle = \langle g^{\beta}(z) \rangle \mathcal{P}^{\beta}(z) ,$$

$$\langle P^{\beta}(z)g^{\beta}(z)P^{\beta}(z) \rangle = \mathcal{P}^{\beta}(z) \langle g^{\beta}(z) \rangle \mathcal{P}^{\beta}(z)$$

$$+ \langle P^{\beta}(z) \rangle - \mathcal{P}^{\beta}(z) ,$$
(A5)

which can be verified by a direct substitution of (A3) into the left-hand sides of Eqs. (A5). Taking the (RL, R'L')elements of matrix equations (A5) and using the fact that $\mathcal{P}^{\beta}(z)$ is the matrix diagonal with respect to the site index but, generally, nondiagonal with respect to the orbital indices L and L', we rewrite (A4) in the form

$$\langle g^{\beta}(z) \rangle_{RL,R'L'}^{AA} = \frac{1}{\Delta P_{L}^{\beta}(z) \Delta P_{L'}^{\beta}(z)} \sum_{L''} \sum_{L'''} \left\{ \left[P_{L}^{\beta,B}(z) \delta_{LL''} - \mathcal{P}_{LL''}^{\beta}(z) \right] \\ \times \langle g^{\beta}(z) \rangle_{RL'',R'L'''} \left[P_{L''}^{\beta,\beta}(z) \delta_{L''L'} - \mathcal{P}_{L''L'}^{\beta}(z) \right] + \left[\langle P_{L}^{\beta}(z) \rangle_{LL'} - \mathcal{P}_{LL'}^{\beta}(z) \right] \right\}$$

$$(A6)$$

The expression (A6) is simplified for cubic lattices, where due to their symmetry the coherent-potential function $\mathcal{P}^{\beta}(z)$ is diagonal with respect to the orbital indices L and L'. Then

$$\langle g^{\beta}(z) \rangle_{RL,R'L'}^{AA} = \frac{1}{\Delta P_L^{\beta}(z) \Delta_{L'}^{\beta}(z)} \{ [P_L^{\beta,B}(z) - \mathcal{P}_L^{\beta}(z)] \langle g^{\beta}(z) \rangle_{RL,R'L'} [P_L^{\beta,B}(z) - \mathcal{P}_L^{\beta}(z)] + [\langle P_L^{\beta}(z) \rangle - \mathcal{P}_L^{\beta}(z)] \delta_{LL'} \delta_{RR'} \} .$$

$$(A7)$$

The results for remaining elements $\langle g^{\beta}(z) \rangle_{RL,R'L'}^{QQ'}$, Q, Q' = A or B, are obtained by changing corresponding indices in (A6) or (A7), and taking care of signs in Eqs. (A2). Consequently, the result given by Eq. (17) is obtained.

The determination of the coherent-potential matrix $\mathcal{P}_{LL'}^{\beta}(z)$ by the configurational averaging of Eq. (14), is obtained in a standard manner, ^{36,34} employing the fact that $P^{\beta}(z)$ is the random, but site-diagonal, matrix and S^{β} is a nonrandom matrix. We obtain, within the CPA,

$$c^{A}\tau_{LL'}^{\beta,A}(z) + c^{B}\tau_{LL'}^{\beta,B}(z) = 0 ,$$

$$\tau_{LL}^{\beta,Q}(z) = ([P^{\beta,Q}(z) - \mathcal{P}^{\beta}(z)]\{1 + \Phi^{\beta}(z)[P^{\beta,Q}(z) - \mathcal{P}^{\beta}(z)]\}^{-1})_{RL,R'L'} , \quad Q = A,B$$

$$\Phi_{LL'}^{\beta}(z) = \frac{1}{N} \sum_{k} \{[\mathcal{P}^{\beta}(z) - S^{\beta}(k)]^{-1}\}_{RL,R'L'} .$$
(A8)

Here, $S_{LL'}^{\beta}(k)$ is the Bloch transform of $S_{RL,R'L'}^{\beta}$, and $P^{\beta,Q}(z)$ is the site- and symmetry diagonal potential-function matrix. Let us remark that the quantities $\mathcal{P}_{LL'}^{\beta}(z)$, $\Phi_{LL'}^{\beta,Q}(z)$, and $\tau_{LL'}^{\beta,Q}(z)$ appearing in (A8) are, due to the single-site approximation used here, independent of the site-index R. The quantities \mathcal{P}^{β} and Φ^{β} are even translationally invariant, and $\tau^{\beta,Q}$ depends on the type Q of atoms at a given site. For cubic lattices, $\mathcal{P}^{\beta}(z)$ and $\Phi^{\beta}(z)$, and hence also $\tau^{\beta,Q}(z)$, are all diagonal matrices with respect to indices L and L'.

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