

Coherent-potential approximation in the tight-binding linear muffin-tin orbital method

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We describe a consistent approach for applying the coherent-potential approximation (CPA) to the various representations of the linear muffin-tin orbital method. Unlike the previous works of Kudrnovský *et al.* [Phys. Rev. B **35**, 2487 (1987); **41**, 7515 (1990)], our results for the ensemble-averaged Green functions in the tight-binding representation yield E - and \mathbf{r} -dependent quantities that are consistent with the traditional applications of the single-site CPA. To illustrate the reliability and the usefulness of our approach we compare the nonspherically averaged charge densities, calculated in real space, of ordered NiPt in $L1_0$ structure and the substitutionally disordered Ni_{0.5}Pt_{0.5} on a face-centered-cubic lattice.

With the development of screening transformations of the linear muffin-tin orbitals (LMTO's) it has become possible to transform the LMTO method,^{1,2} a reliable and computationally efficient approach for calculating the electronic structures of periodic solids, into a *first-principles* tight-binding (TB) LMTO method.³⁻⁵ One of the advantages of the TB approach is the possibility of describing the electronic structures of systems without perfect translational symmetry such as surfaces,⁶ interfaces,⁷ dilute impurities,⁸ and others. So far the applications of the LMTO-based approaches have been mostly directed towards ordered systems with or without perfect translational symmetry, although efforts are being made to describe amorphous solids⁹ using the TB LMTO formalism.

To be able to incorporate some of the advantages that the TB LMTO method offers in the electronic structure description of substitutionally disordered systems, we have to take into account the effects of substitutional disorder within the LMTO framework. As the coherent-potential approximation (CPA), in conjunction with Korringa-Kohn-Rostoker (KKR) method, has been very successful in describing the effects of substitutional disorder,¹⁰⁻¹² the application of the CPA in the context of the TB LMTO method is expected to be reliable as well.

Generally, the electronic properties of substitutionally disordered alloys are calculated from the ensemble-averaged Green functions, $G^C(E, \mathbf{r}, \mathbf{r}')$, obtained within the single-site CPA.¹⁰⁻¹³ The ensemble averaging of the Green functions depends crucially on whether E - and \mathbf{r} -dependent quantities are single site or multisite in nature. For example, the \mathbf{r} dependence of $G^C(E, \mathbf{r}, \mathbf{r}')$ in *empirical* TB or *first-principles* KKR-CPA-type approaches comes through the basis functions, taken to be atomiclike functions or partial waves, respectively, which are single site in nature. That is, these basis functions are determined entirely by the characteristics of the atom at that site, although the characteristics themselves may depend implicitly on the surrounding medium. However, in the

first-principles TB LMTO method the basis functions are multisite in nature,³⁻⁵ i.e., they depend explicitly on the surrounding atoms. Thus one has to be careful in applying the ensemble-averaged results of empirical TB or KKR-CPA-type approaches to the TB LMTO method.

Previous attempts^{14,15} at incorporating the CPA within the TB LMTO approach do not properly take into account the multisite nature of the TB LMTO's. As a consequence, the ensemble-averaged Green functions for the substitutionally disordered alloys become inconsistent with the traditional applications of the single-site CPA. In other words, the calculation of the single-site wave functions relies on specific configurations of the neighboring atoms, which is inconsistent with the single-site CPA. These inconsistencies lead to erroneous charge density, $\rho^C(\mathbf{r})$, and other \mathbf{r} -dependent quantities calculated from $G^C(E, \mathbf{r}, \mathbf{r}')$.

In this paper we describe a consistent approach for applying the CPA to the various representations of the LMTO method. In particular, we find that the application of the single-site CPA to the TB representation requires an additional approximation, missing in previous works.^{14,15} We illustrate the usefulness of our approach by calculating in real space the nonspherically averaged charge densities of ordered NiPt in $L1_0$ structure and the substitutionally disordered Ni_{0.5}Pt_{0.5} on a face-centered-cubic (fcc) lattice. In the following we concentrate on that part of the Green function that contributes to the charge density, although our results can be easily extended to include terms that are left out. The details of our derivations are given in Ref. 16, and the full expression for the Green functions is derived in Ref. 17. The two main references that we use are Refs. 5 and 10.

An energy-independent LMTO in a general representation α can be written as^{5,16}

$$\chi_{RL}^{\alpha}(\mathbf{r}_R) = \phi_{RL}^{\alpha}(\mathbf{r}_R) + \sum_{R'L'} \phi_{R'L'}^{\alpha}(\mathbf{r}_{R'}) h_{R'L',RL}^{\alpha} + \chi_{RL}^{\alpha,i}(\mathbf{r}_R), \quad (1)$$

where $\mathbf{r}_R = \mathbf{r} - \mathbf{R}$, \mathbf{R} are the site vectors, and L ($\equiv lm$) denotes the angular momentum index. The functions $\phi_{RL}^\alpha(\mathbf{r}_R)$, $\dot{\phi}_{RL}^\alpha(\mathbf{r}_R)$, and $h_{R'L',RL}^\alpha$ are defined in Ref. 5, and $\chi_{RL}^{\alpha,i}(\mathbf{r}_R)$ are the solutions of the Laplace equation in the interstitial region. In Eq. (1) as well as in the following, we set $E = E_\nu$ and do not indicate energy dependence explicitly. An overdot indicates derivative with respect to energy. The values of α determine the spatial extent of the LMTO's through the structure constant term in h^α . For $\alpha_{Rl} = 0$ for each R and l , the structure constants are long ranged leading to extended $\chi_{RL}^0(\mathbf{r}_R)$. The choice of $\alpha_{Rl} = \gamma_l$,⁵ known as the

nearly orthogonal representation, results in exponentially damped structure constants, and hence relatively localized $\chi_{RL}^\gamma(\mathbf{r}_R)$. The representation obtained for $\alpha_{Rl} = \beta_l$, with $\beta_s = 0.3485$, $\beta_p = 0.05303$, and $\beta_d = 0.0107$, is called the TB representation⁵ in which the structure constants are vanishingly small after second- or third-nearest neighbors for close-packed solids. The β representation is well suited for real-space evaluation of the charge densities because of the localized nature of the TB LMTO's.

The Green function of ordered structures can be expressed in terms of the LMTO's as¹⁶

$$G^\alpha(E, \mathbf{r}, \mathbf{r}) = \sum_{li} J_{Rli}^\alpha(E, \mathbf{r}_R, \mathbf{r}_R) + \sum_{R'L'} \sum_{RL} \chi_{R'L'}^\alpha(\mathbf{r}_{R'}) [\dot{P}_{R'l'}^\alpha(E)]^{(1/2)} \times [\Sigma_{R'L',RL}^\alpha(E) - 1/P_{Rl}^\alpha(E)] [\dot{P}_{Rl}^\alpha(E)]^{(1/2)} \chi_{RL}^\alpha(\mathbf{r}_R), \quad (2)$$

where Σ^α is the atomic-sphere approximation (ASA) version of the scattering path operator and is defined in Refs. 16, 18, and 19. The single-scatterer Green function, $J_{Rli}^\alpha(E, \mathbf{r}, \mathbf{r})$, is given by¹⁸

$$J_{Rli}^\alpha(E, \mathbf{r}, \mathbf{r}) = \frac{\phi_{Rli}(c_{Rli}^\alpha, \mathbf{r}, \mathbf{r}) \phi_{Rli}(c_{Rli}^\alpha, \mathbf{r}, \mathbf{r})}{E - c_{Rli}^\alpha}. \quad (3)$$

The resonance energies c_{Rli}^α 's are determined from the potential function $P^\alpha(E)$ such that $P_{Rl}^\alpha(E = c_{Rli}^\alpha) = 0$, and correspond to the eigenstates, numbered by li ($i = 0, 1, 2, \dots$), of the single scatterer. However, in practice the sum over li is carried through only for the valence states and hence in the following we drop the symbol i .

For describing the electronic structure of substitutionally disordered alloys made of atoms of type A and B , we associate with each lattice point a coherent-potential function, $P_L^{\alpha,C}(E)$, determined self-consistently from the relation

$$P_L^{\alpha,C}(E) = C_A P_L^{\alpha,A}(E) + C_B P_L^{\alpha,B}(E) + \{P_L^{\alpha,A}(E) - P_L^{\alpha,C}(E)\} \times \Sigma_{L'L}^\alpha \{P_L^{\alpha,B}(E) - P_L^{\alpha,C}(E)\}, \quad (4)$$

where C_A and C_B are the concentrations of A and B atoms, respectively, and we have assumed the lattice to be cubic with $l \leq 2$. For $l > 2$ or for the case of noncubic lattices for all l , the matrices in Eq. (4) are not diagonal and a more general expression should be used as given in Ref. 10. Equation (4) is the formal analogue of the expansion determining the effective scattering matrix in KKR CPA. The electronic properties of such alloys are calculated with the help of Green functions, which are ensemble averages of the Green functions given by Eq. (2), and the understanding that the effective scatterers correspond to the coherent-potential function given by Eq. (4).

The process of taking the ensemble average of Green

functions within the single-site CPA, relevant for our purposes, is described in detail in Refs. 10 and 11. In order to apply the results of Ref. 10, we must first ensure that the individual terms of the Green functions given by Eq. (2) are similar in nature to the terms in the Green functions of Ref. 10 as far as the process of ensemble averaging is concerned. The Green function given by Eq. (2) has two multisite terms, namely, the scattering path operator Σ^α and the LMTO χ^α . As pointed out earlier, the function Σ^α is the ASA version of the scattering path operator of the multiple-scattering theory and thus during ensemble averaging can be treated exactly like τ of Ref. 10. We note that for $\alpha_{Rl} = \gamma_{Rl}$, the structure constants S^γ become random and hence Σ^γ is not easily amenable to the ensemble averaging within the single-site CPA. Even if we were to treat the disorder in the structure constants along the lines suggested by Blackman, Esterling, and Berk,¹³ ambiguities in the construction of the site wave function itself would remain. One approach would be to average the wave function over all possible occupations of neighboring sites, thus, replacing $\phi_{RL}^\alpha(\mathbf{r}_R)$ in Eq. (1) by its concentration average. However, averaging the wave function is inconsistent with the CPA. A convenient way out is to use the scaling relations given by Eq. (91) of Ref. 5, and write Σ^γ in terms of Σ^0 or Σ^β .

The multisite nature of χ^α prevents us from applying directly the results of Ref. 10. From Eq. (1) we see that in the α representation the LMTO at \mathbf{R} has contributions coming from its neighbors situated at \mathbf{R}' . These contributions depend not only on the structure constants but also on the radial functions and the potential parameters of atoms surrounding \mathbf{R} . In the CPA this prescription for evaluating χ^α cannot be carried out because CPA replaces the individual atoms by effective atoms whose radial functions and potential parameters are unknown. Thus, to be consistent with the traditional applications of the CPA, we make χ^α site diagonal so that the ensemble average of the Green functions can be carried out using the procedure outlined in Ref. 10. As shown in Refs. 5 and 16, the χ^α 's become site-diagonal in pure- L

approximation. Thus, in Eq. (1) the summation over R' is restricted to the site in question. Hence, in the following we evaluate the ensemble-averaged Green functions within the pure- L approximation and for site-diagonal χ^{α} 's.

$$G_{RL',RL}^{\alpha,C,on}(E, \mathbf{r}, \mathbf{r}) = C_A J_{RI}^{\alpha,A}(E, \mathbf{r}_R, \mathbf{r}_R) + C_A \chi_{RL'}^{\alpha,A}(\mathbf{r}_R) [\dot{P}_{RI}^{\alpha,A}(E)]^{(1/2)} \\ \times [D_{RL',RL}^{\alpha,A}(E) \Sigma_{RL',RL}^{\alpha}(E) - 1/P_{RI}^{\alpha,A}(E)] [\dot{P}_{RI}^{\alpha,A}(E)]^{(1/2)} \chi_{RL}^{\alpha,A}(\mathbf{r}_R) \\ + C_B J_{RI}^{\alpha,B}(E, \mathbf{r}_R, \mathbf{r}_R) + C_B \chi_{RL'}^{\alpha,B}(\mathbf{r}_R) [\dot{P}_{RI}^{\alpha,B}(E)]^{(1/2)} \\ \times [D_{RL',RL}^{\alpha,B}(E) \Sigma_{RL',RL}^{\alpha}(E) - 1/P_{RI}^{\alpha,B}(E)] [\dot{P}_{RI}^{\alpha,B}(E)]^{(1/2)} \chi_{RL}^{\alpha,B}(\mathbf{r}_R),$$

where

$$D_{nL',nL}^{\alpha,n} = [\delta_{L'L} + \Sigma_{0L',0L}^{\alpha}(E) \{P_I^{\alpha,n}(E) - P_L^{\alpha,C}(E)\}]_{nL',nL}^{-1}, \quad (6)$$

the superscript C stands for the single-site ensemble-averaged Green functions, and the central site is denoted by $R = 0$. The ensemble-averaged off-site Green function becomes

$$G_{R'L',RL}^{\alpha,C,off}(E, \mathbf{r}_R, \mathbf{r}_{R'}) = \{C_A \chi_{R'L'}^{\alpha,A}(\mathbf{r}_{R'}) [\dot{P}_{R'I'}^{\alpha,A}(E)]^{(1/2)} D_{R'L',R'L'}^{\alpha,A}(E) + C_B \chi_{R'L'}^{\alpha,B}(\mathbf{r}_{R'}) [\dot{P}_{R'I'}^{\alpha,B}(E)]^{(1/2)} D_{R'L',R'L'}^{\alpha,B}(E)\} \\ \times [\Sigma_{R'L',RL}^{\alpha}(E)] \{C_A \chi_{RL}^{\alpha,A}(\mathbf{r}_R) [\dot{P}_{RI}^{\alpha,A}(E)]^{(1/2)} D_{RL,RL}^{\alpha,A}(E) \\ + C_B \chi_{RL}^{\alpha,B}(\mathbf{r}_R) [\dot{P}_{RI}^{\alpha,B}(E)]^{(1/2)} D_{RL,RL}^{\alpha,B}(E)\}. \quad (7)$$

Equations (5) and (7) represent the ensemble-averaged Green functions for the substitutionally disordered alloys in the CPA.

As expected, use of $\alpha_{RI} = 0$, and the partial waves in Eqs. (5) and (7) lead to the results of Refs. 20–22. If we further assume that the potential parameter p^γ is negligible, the densities of states calculated from Eq. (5) are similar to the results of Refs. 14 and 15 because the imaginary part of the Green function is representation invariant.⁵ However, the ensemble-averaged Green functions given by Eqs. (5) and (7) provide expression for the full nonspherical charge density over *all* of \mathbf{r} space.

In the β representation Eqs. (5) and (7) can be used to calculate the electronic properties of disordered systems in real space. For example, the nonspherically averaged total charge density in the CPA is given by

$$\rho^C(\mathbf{r}) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^{E_F} \left[\sum_{RL'L} G_{RL',RL}^{\beta,C,on}(E, \mathbf{r}_R, \mathbf{r}_R) \right. \\ \left. + \sum_{R'L'} \sum_{RL} G_{R'L',RL}^{\beta,C,off}(E, \mathbf{r}_R, \mathbf{r}_{R'}) \right], \quad (8)$$

where E_F is the alloy Fermi energy. For evaluating $\rho^C(\mathbf{r})$ for the substitutionally disordered alloys using Eq. (8) we use the pure- L TB LMTO's.^{5,16} The evaluation of pure- L TB LMTO's at site \mathbf{R} requires the radial solutions inside the atomic sphere, the potential parameters associated with the atomic sphere at \mathbf{R} , and the on-site terms $h_{RL,RL}^{\beta}$, and thus presents no ambiguities with regards to the ensemble averaging of the Green functions for the substitutionally disordered alloys.

We have tested our method by calculating the valence

The ensemble-averaging of the Green function can be easily carried out if we express it in terms of an on-site contribution, $G_{RL',RL}^{\alpha,on}(E, \mathbf{r}, \mathbf{r})$, and of an off-site contribution, $G_{R'L',RL}^{\alpha,off}(E, \mathbf{r}, \mathbf{r})$. We find that the ensemble-averaged on-site Green function is given by

charge densities of ordered structures where we find that our approach yields charge densities that are essentially identical to the results of the full-potential methods. Results for Si, Al, Li, and AlLi in $L1_0$ phase are given in Ref. 16. We also find that the use of pure- L TB LMTO's for calculating the charge densities of ordered structures leads to the piling up of charge along the nearest-neighbor directions.

To illustrate the usefulness of our approach, we show in Fig. 1 the nonspherically averaged charge densities of

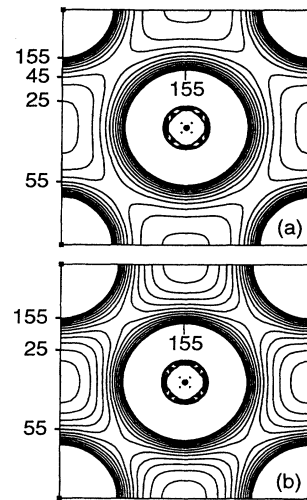


FIG. 1. The valence charge densities of (a) $L1_0$ NiPt in the (100) plane and (b) substitutionally disordered $\text{Ni}_{0.5}\text{Pt}_{0.5}$ in the (001) plane of the fcc lattice calculated scalar relativistically. The filled circles denote Pt atoms, and the filled squares denote Ni atoms in (a) and CPA atoms in (b). The charge density is in 10^3 a.u.

ordered NiPt and substitutionally disordered $\text{Ni}_{0.5}\text{Pt}_{0.5}$ calculated using the pure- L TB LMTO's from the spherically symmetric one-electron potentials obtained for ordered NiPt and disordered $\text{Ni}_{0.5}\text{Pt}_{0.5}$, respectively. The charge density of ordered NiPt, shown in Fig. 1(a), is almost entirely spherically symmetric except along the Ni-Ni directions. In Fig. 1(b) we show the nonspherically averaged charge density for the substitutionally disordered $\text{Ni}_{0.5}\text{Pt}_{0.5}$ in the (001) plane of the fcc lattice with the Pt atom at the central site surrounded by CPA atoms. A comparison of Figs. 1(a) and 1(b) reveals that up to Pt atomic sphere the changes in the charge density due to substitutional disorder are small. Some of the differences in $\rho(\mathbf{r})$ of NiPt and $\text{Ni}_{0.5}\text{Pt}_{0.5}$, as we move away from the central site, are due to the fact that in the disordered case the central site (Pt) is surrounded

by CPA atoms and not by Ni atoms as in NiPt.

In conclusion, we have applied the CPA to the various representations of the LMTO method, including the TB representation. The resulting ensemble-averaged Green functions require the TB LMTO's to be site diagonal, otherwise the \mathbf{r} -dependent quantities become inconsistent with the traditional applications of the single-site CPA. We have demonstrated the usefulness of our approach by calculating in real space the nonspherically averaged charge density of substitutionally disordered $\text{Ni}_{0.5}\text{Pt}_{0.5}$ on a fcc lattice and compared it with the charge density of ordered NiPt in $L1_0$ structure.

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