Application of Coherent-Potential Approximation to Disordered Muffin-Tin Alloys

A. Bansil

Physics Department, Northeastern University, Boston, Massachusetts 02115

(Received 12 April 1978; revised manuscript received 14 November 1978)

I report implementation of the coherent-potential approximation for obtaining the electronic density of states and component charge densities in disordered muffin-tin alloys. Illustrative results for Cu$_x$Ni$_{1-x}$ are presented. The extent to which the self-consistency in treating disorder influences the electronic spectrum is considered.

It has become clear in the recent years that, in order to obtain a realistic description of the electronic spectrum of disordered transition- and noble-metal alloys, the atomic potentials must be treated within the framework of the muffin-tin model, as is usually done for the corresponding perfect crystals, and that the simple one- and two-band tight-binding model Hamiltonians are not adequate in these cases. In this connection, two of the most commonly used approximations have been the coherent-potential approximation (CPA) and the average $t$-matrix approximation (ATA). Of the two, the CPA treats the disorder self-consistently and is to be preferred. The attractiveness of the ATA derives from its relative simplicity in application to realistic models. In spite of the significant progress made with regard to the application of these two approximations to the muffin-tin Hamiltonian, difficulties have persisted with each of the schemes. The CPA formalism is well developed, but its practical implementation to the muffin-tin Hamiltonian has not been possible because of the difficult and repeated Brillouin-zone integrations necessary to solve the CPA self-consistency equation. By contrast, the difficulties with the ATA are formal in nature: Although the currently used ATA expression for the average density of states $\langle \rho(E) \rangle$ gives reasonable results in all instances studied so far, the corresponding expressions for the component densities $\langle \rho_{AB}(E) \rangle$ (i.e., the electronic charge densities associated
with the neighborhood of the A and B atoms in the alloy yield negative results in many cases, and are not reliable.\textsuperscript{3}

In this Letter, I show how the calculation of the CPA spectrum can be made tractable in disordered muffin-tin alloys by using the special-directions method of \( k \)-space integration\textsuperscript{8} to solve the muffin-tin CPA equation. The question of handling the free-electron poles in the CPA expression for the A- and B-component densities of states is taken up. I have also developed a new version of the ATA\textsuperscript{7} which, however, will not be discussed here, except insofar as this new ATA can be viewed as the lowest-order approximation to the full CPA solution and, therefore, its comparison with the CPA tells us the extent to which the self-consistency influences the electronic spectrum.

The random substitutional binary alloy \( A_\mathrm{y}B_\mathrm{1-x} \) will be discussed within the framework of the one-electron Hamiltonian

\[
H = \frac{p^2}{2m} + \sum_n v_n^{A(B)}(r).
\]

Here, the crystal potential is assumed to be given as the sum of nonoverlapping, spherically symmetric, muffin-tin atomic potentials \( v_n^{A(B)}(r) \equiv v_n^{A(B)}(|\vec{r} - \vec{R}_n|) \), centered on the atomic sites \( \{ \vec{R}_n \} \).

By going into the angular momentum representation, and using the familiar multiple-scattering-theory techniques,\textsuperscript{1} we can study the properties of the disordered alloys on the basis of the muffin-tin Hamiltonian (1). Without presenting details, I quote the relevant expressions for the CPA spectrum\textsuperscript{14,16}:

\[
\langle \rho(E) \rangle^{\text{CPA}} = \rho_0(E) - \frac{1}{\pi N} \text{Im} \sum_k \left[ \left( 1 - T_{00}^{\text{CPA}}(\tau_{\text{CPA}}^{-1} - \tau_A^{-1}) \right) \frac{d\tau_A^{-1}}{dE} + \left( 1 - T_{00}^{\text{CPA}}(\tau_{\text{CPA}}^{-1} - \tau_B^{-1}) \right) \frac{d\tau_B^{-1}}{dE} \right]
\]

\[
\langle \rho_A(E) \rangle^{\text{CPA}} = \rho_0(E) - \frac{1}{\pi N} \text{Im} \sum_k \left[ \left( 1 - T_{00}^{\text{CPA}}(\tau_{\text{CPA}}^{-1} - \tau_A^{-1}) \right) \frac{d\tau_A^{-1}}{dE} \right]
\]

\[
\langle \rho_B(E) \rangle^{\text{CPA}} = \rho_0(E) - \frac{1}{\pi N} \text{Im} \sum_k \left[ \left( 1 - T_{00}^{\text{CPA}}(\tau_{\text{CPA}}^{-1} - \tau_B^{-1}) \right) \frac{d\tau_B^{-1}}{dE} \right]
\]

with \( \langle \rho_{A(B)}(E) \rangle^{\text{CPA}} \) obtained from (3) by interchanges \( A \rightarrow B \) and \( x \rightarrow y (= 1 - x) \). Here \( \rho_0(E) \) denotes the free-electron density of states, and \( N \) the number of atoms in the crystal. \( L \equiv (l, m) \) is a composite angular momentum index including both orbital and magnetic quantum numbers. \( B_{\mu}(E) \) is the matrix of usual Korringa-Kohn-Rostoker (KKR) structure functions. \( \tau_{\mu}, \tau_{B\mu}, \text{ and } \tau_{\text{CPA}}, \text{ respectively, are on-the-energy-shell matrix elements of the } A, B, \text{ and effective coherent-potential scattering operators.}

These are related to the phase shifts \( \delta_{\mu}^{A(B)} \) via the familiar equation

\[
[\tau_{A(B)}(E)]_1 = -E^{-\mu} \exp[i\delta_{\mu}^{A(B)}(E)] \sin\delta_{\mu}^{A(B)}(E).
\]

The quantities \( T_{00}^{\text{CPA}} \) are defined by

\[
T_{00}^{\text{CPA}}(E) = \frac{1}{N} \sum_k \left[ \frac{1}{\tau_{\text{CPA}}^{-1} - B_{\mu}(E)} \right],
\]

which is implicitly a matrix equation in the angular momentum \( (L) \) space. The \( \vec{k} \) summations in Eqs. (2), (3), and (5) only extend over the first Brillouin zone. The effective CPA scattering amplitudes, \( \tau_{\text{CPA}} \), are given by the self-consistency equation\textsuperscript{8}

\[
\tau_{\text{CPA}}^{-1} = x\tau_A^{-1} + y\tau_B^{-1} + (\tau_{\text{CPA}}^{-1} - \tau_A^{-1})T_{00}^{\text{CPA}}(\tau_{\text{CPA}}^{-1} - \tau_B^{-1}).
\]

Equation (2) shows that the peaks in the spectral function \( \langle \rho(\vec{k}, E) \rangle^{\text{CPA}} \) [defined by the second quality in Eq. (2)] come not only from the complex zeros of the secular equation

\[
\| \tau_{\text{CPA}}^{-1} - B_{\mu}(E) \| = 0
\]

but also from those of

\[
\| 1 - T_{00}^{\text{CPA}}(\tau_{\text{CPA}}^{-1} - \tau_{A(B)}^{-1}) \| = 0.
\]

An equation similar to (7) has been discussed extensively in connection with the ATA for muffin-tin alloys.\textsuperscript{2,3} Note, that for a perfect \( A \) (\( B \)) crys-
tal \( \tau_{\text{CPA}} - \tau_{\text{A}(B)} \) and (7) reduces to the familiar KKR equation of band theory of perfect crystals. Therefore, this equation can be viewed as representing Bloch-like states in an ordered medium of \( \tau_{\text{CPA}} \) atoms. By contrast, Eq. (8) possesses no simple analogy with a perfect crystal and, to my knowledge, has not been discussed previously in connection with disordered alloys. In the limit of \( x \) (or \( y \) \( \rightarrow 0 \), \( \tau_{\text{CPA}} - \tau_{B} \) (or \( \tau_{A} \)), and Eq. (8) is easily shown to yield the real impurity levels for an \( A \) (or \( B \)) atom embedded in an otherwise perfect \( B \) (or \( A \)) crystal. In general, therefore, Eq. (8) may be viewed as representing the impurity-like levels arising when a single \( A \) (or \( B \)) atom is placed in the coherent-potential medium. I emphasize that the impurity states given by Eq. (8) are non-Bloch-type in nature, and their appearance in the alloy is a characteristic effect of disorder.

The basic difficulty in solving the CPA equation (6) arises from the fact that to solve this equation the quantity \( T_{\infty}^{\text{CPA}}(E) \) given by Eq. (5) must be evaluated repeatedly. Since the integrand in the Brillouin-zone summation in Eq. (5) generally possesses sharp structures associated with the Bloch-type solutions of Eq. (7), the conventional methods of \( k \)-space integration are not effective. However, the special-direction method\(^6\) is applicable. Using this technique, I have solved the CPA equation in \( \text{Cu}_{x}\text{Ni}_{1-x} \) and \( \text{Cu}_{x}\text{Zn}_{1-x} \) for a range of alloy compositions. The energy dependence of \( \tau_{\text{CPA}}(E) \) is found to be insensitive to whether thirteen\(^{6} \) or twenty-one\(^{9} \) or even larger sets\(^{10} \) of special directions are used to evaluate \( T_{\infty}^{\text{CPA}}(E) \). Our experience is that the thirteen-direction set would be adequate for solving the CPA equation in transition- and noble-metal alloys in most cases.\(^{11} \)

We note that the free-electron singularities arising from the \( dB_{\gamma}/dE \) term in the component density-of-states formula (3) do not cancel against those coming from \( \rho_{p}(E) \) terms. The \( \langle \rho_{A(B)}(E) \rangle \) expression involves this essential added degree of complexity, which is not present in the \( \langle \rho(E) \rangle \) computations. I have handled this problem by fitting each of the diagonal elements of the integrand in Eq. (3) by a function of the form const/[\( E - (\mathbf{K} + \mathbf{K}_{n})^{2} \)] in the vicinity of \( E = (\mathbf{K} + \mathbf{K}_{n})^{2} \) (\( \mathbf{K}_{n} \) denotes a reciprocal lattice vector) and then evaluating the contribution of the singular part analytically. It is noteworthy that if the free-electron singularities are not treated properly, grossly incorrect results for \( \langle \rho_{A(B)}(E) \rangle \) can result.

Some illustrate results for \( \tau_{\text{CPA}}(E) \) and the densities of states are now presented. The energy dependence of the \( l = 2 \) scattering phase shifts in \( \text{Cu}_{0.75}\text{Ni}_{0.25} \) on the basis of the muffin-tin potentials used in Ref. 3 is shown in Fig. 1. The \( s \)- and \( p \)-phase shifts for \( \text{Cu}, \text{Ni}, \) and the alloy are quite similar and vary slowly in the energy regime of present interest and are not considered. Because of the cubic symmetry of the average alloy, the \( d \) phase shifts in the CPA for states of symmetry \( t_{2g} \) and \( e_{g} \) are seen to be different. This distinction, however, does not apply to the ATA scatterer \( \langle \tau \rangle = x\tau_{A} + (1-x)\tau_{B} \), which is spherically symmetric (shown as dot-dashed curves). Figure 1 shows that the peaks in the real as well as the imaginary parts of \( \sin \delta_{a} \) arising from Ni impurities (marked by arrows) are shifted to higher energies by roughly 0.05 Ry in the CPA compared to the ATA.\(^{12} \) We find such differences in the positions of the impurity peaks more generally between the two approximations in the Cu-rich as well as the Ni-rich alloys.

In discussion of the CPA results in Fig. 2, the focus is on delineating the importance of self-consistency in electronic spectra computations.
In disordered muffin-tin alloys. The dashed curves in this figure have been obtained by replacing \( \rho_{\text{CPA}} \) by \( \tau A \times x \) in Eqs. (2) and (3) and represent the lowest-order approximations to the full CPA results. (Since they employ \( \tau I \), the dashed curves in Fig. 2 are labeled as ATA. This new ATA, however, differs significantly from the commonly used version of the ATA, and will be discussed elsewhere. A comparison of the solid and the dashed curves in Fig. 2 reveals that, aside from larger overall smoothing, self-consistency causes no significant changes in the locations or widths of the spectra.

In view of Fig. 2 and additional calculations that I have carried out for other compositions in \( \text{Cu}_{0.75}\text{Ni}_{0.25} \) and \( \text{Cu}_{0.75}\text{Zn}_{0.25} \), I conclude that self-consistency in solving the muffin-tin CPA equations is not likely to be very important in discussing many aspects of the electronic spectra of transition- and noble-metal alloys.

I am very grateful to Dr. P. N. Argyres, Dr. R. Prasad, and Dr. L. Schwartz for many important conversations. This work was supported in part by the National Science Foundation.

\[ \text{FIG. 2. The CPA and ATA spectra in } \text{Cu}_{0.75}\text{Ni}_{0.25} \text{ and } \text{Cu}_{0.75}\text{Zn}_{0.25}. \text{ The ATA curves represent the lowest-order approximation to the full CPA results.} \]

\[ \text{References:} \]

5. The first muffin-tin CPA calculations of \( \rho(E) \) were reported in \( \text{CuNi}_{1-x} \) by G. M. Stocks, B. L. Gyorffy, and W. M. E. Temmerman [Bull. Am. Phys. Soc. 23, 516 (1978), and Phys. Rev. Lett. 41, 339 (1978)] and by A. Bansil [Bull. Am. Phys. Soc. 25, 260 (1978), and the present article]. In this regard, the results of Stocks, Gyorffy, and Temmerman and of Bansil are in agreement. However, Stocks, Gyorffy, and Temmerman do not consider CPA component densities of states.
7. A. Bansil, to be published.
10. R. Prasad and A. Bansil, to be published.
11. To gain efficiency in computations, the scheme of A. R. Williams, J. F. Janak, and V. L. Moruzzi [Phys. Rev. B 6, 4509 (1972)] was used to evaluate KKR structure functions and their derivatives occurring in Eqs. (2), (3), and (5).
12. This effect was also observed in approximations to \( \tau \) in \( \text{CuNi}_{1-x} \) reported by Stocks et al. [J. Phys. F 7, 1859 (1977)].