Correlated electronic structure with uncorrelated disorder

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We introduce a computational scheme for calculating the electronic structure of random alloys that includes electronic correlations within the framework of the combined density functional and dynamical mean-field theory. By making use of the particularly simple parameterization of the electron Green’s function within the linearized muffin-tin orbitals method, we show that it is possible to greatly simplify the embedding of the self-energy. This in turn facilitates the implementation of the coherent potential approximation, which is used to model the substitutional disorder. The computational technique is tested on the Cu-Pd binary alloy system, and for disordered Mn-Ni interchange in the half-metallic NiMnSb.

I. INTRODUCTION

Disordered metallic alloys find applications in a large number of areas of materials science. Designing alloys with specific thermal, electrical, and mechanical properties such as conductivity, ductility, and strength, nowadays commonly starts at the microscopic level. First-principles calculations of the electronic structure offer a parameter-free framework to meet specific engineering demands for materials prediction. Advances in the atomistic simulation of physical properties should to a large extent be attributed to the development of density functional theory (DFT) within the local density approximation (LDA) or beyond-LDA schemes.

In solids exhibiting disorder the calculation of any physical property involves configurational averaging over all realizations of the random variables characterizing the disorder. In the case of substitutional disorder the symmetry of the lattice is kept, but the type of atoms in the basis is randomly distributed. This causes the crystal to lose translational symmetry, making the Bloch theorem inapplicable. Perhaps the most successful approach to solve the problems associated with substitutional disorder is the coherent potential approximation (CPA). The presence of random atomic substitution generates a fluctuating external potential within which the CPA is substituted by an effective medium. This effective medium is energy dependent and is determined self-consistently through the condition that the impurity scattering should vanish on average. The CPA is a single-site approximation, which becomes exact in certain limiting cases. The explanation for the good accuracy of the CPA can be traced back to the fact that it becomes exact in the limit of infinite lattice coordination number, $Z \rightarrow \infty$.

The CPA was initially applied to tight-binding Hamiltonians where for binary alloys the CPA equations take a complex polynomial form that can be solved directly. Later Györrfy formulated the CPA equations for the muffin-tin potentials within the multiple-scattering Korringa-Kohn-Rostocker (KKR) method. Consequently, the configurational average could be performed over the scattering path operator, instead of the Green’s function, simplifying the implementation of the CPA for materials calculations. Later the CPA was also implemented within the linearized muffin-tin orbitals (LMTO) basis set. With the advent of the third-generation exact muffin-tin orbitals (EMTO) method, and the full-charge density (FCD) technique, it was possible to go beyond the atomic-sphere approximation (ASA) with CPA calculations and investigate the energetics of anisotropic lattice distortions. For interacting model Hamiltonians, dynamical mean-field theory (DMFT) was also combined with the CPA. Later on the methodology was extended to study realistic materials containing significant electronic correlations within the framework of a combined DFT+DMFT method. To treat weak disorder within the framework of charge self-consistent LDA+DMFT, the CPA has been implemented within the KKR method. In an alternative approach, the band structures computed from DFT were mapped to tight-binding model Hamiltonians where the disorder was treated within the CPA.

In this paper, we introduce a method that can treat substitutional disorder effects through the CPA, and electronic correlation effects through DMFT, on an equal footing for real materials. The method is based on the LDA+DMFT method, $\omega$MTO+DMFT, which was recently introduced by ur. By making use of the particularly simple parameterized form of the electron Green’s function in a linearized basis set, we show that the self-energy can be incorporated naturally within the LMTO formalism as a modification of a single, self-consistently determined parameter. Due to this straightforward inclusion of the many-body effects, the CPA within the
The energy-independent linearized muffin-tin orbitals $\chi_{RL}(r)$, centered at the lattice site $R$, are given as:

$$
\chi_{RL}(r) = \phi_{RL}(r) + \sum_{R' L'} \phi_{RL'}^\ast(r_R) h_{RL,R'L'}^\alpha,
$$

where $h_{RL,R'L'}^\alpha$ are the potential functions, while Sec. III C demonstrates how the electronic self-energy can be incorporated into the LMTO theory. The expansion coefficients $h^\alpha$ are determined from the condition that the wave function is continuous and differentiable at the sphere boundary.

The standard approach adopted in first-principles electronic structure calculations is the mapping to an effective one-particle potential, consistent description for the effective one-particle potential functions, while Sec. III C demonstrates how the potential functions are used as an effective medium for the CPA. Sec. III B shows how the potential functions, while Sec. III C demonstrates how the potential functions are used as an effective medium for the CPA.
where \( z \) is an arbitrary complex energy. Further important relations among the LMTO representations can be found in Appendix A.

### III. ELECTRONIC CORRELATIONS AND DISORDER: THE SINGLE-SITE APPROXIMATION

In this section we present an LMTO-CPA scheme, that allows to include local self-energies, on the level of DMFT, for the alloy components. The scheme is implemented within the Matsubara representation, and is combined with the \( z \)MTO+DMFT method. Section II A briefly discusses the configurational averaging and the CPA, while in Sec. II B we show how DMFT through the Dyson equation leads to a renormalization of the parameters of the LMTO-ASA formalism. Section II C combines the ideas of the previous two sections, and proposes a combined CPA and DMFT loop.

#### A. Configuration averaging and the CPA

In disordered systems the configurational degrees of freedom characterizing the composition are described by a random variable. Consequently, the potentials at sites are random in space as in quenched disordered solids. A particular realization of the random variable constitutes a configuration of the system in discussion. According to Anderson only physically measurable quantities such as diffusion probabilities, response functions, and densities of states should be configurationally averaged. As these quantities are themselves Green’s functions, electronic structure methods using Green’s functions are favored for the study of disordered systems.

A major development of the theory of disordered electronic systems was achieved using the CPA. The CPA belongs to the class of mean-field theories according to which the properties of the entire material are determined from the average behavior at a subsystem, usually taken to be a single site (cell) in the material. In the multiple scattering description of a disordered system, one considers the propagation of an electron through a disordered medium as a succession of elementary scatterings at the random atomic point scatterers. In the single-site approximation one considers only the independent scattering off different sites and finally takes the average over all configurations of the disordered system consisting of these scatterers. One may then consider any single site in a specific configuration and replace the surrounding material by a translationally invariant medium, constructed to reflect the ensemble average over all configurations. In the CPA this medium is chosen in a self-consistent way. One assumes that averages over the occupation of a site embedded in the effective medium yield quantities indistinguishable from those associated with a site of the medium itself.

In view of the great progress achieved through the previous implementations of the CPA within muffin-tin orbitals methods, we present here in detail a novel combination of CPA+DMFT in the recently developed \( z \)MTO+DMFT method.

#### B. Self-energy-modified effective potential parameters

To deal with the important question concerning the effect of interaction, we start by observing that within the DMFT the self-energy is local and primarily modifies the local parameters of the model that describes disorder. In this section, we show that the presence of a local self-energy, \( \Sigma_{RLRL'}(z) \), modifies the potential function \( P \) entering in the expression of the Green’s function in the LMTO-ASA formalism.

We start from the Dyson equation used to construct the LDA+DMFT Green’s function:

\[
[G_{RLRL'}^{\text{DMFT}}(k,z)]^{-1} = [G_{RLRL'}^{\text{LDA}}(k,z)]^{-1} - \Sigma_{RLRL'}(z),
\]

(10)

where \( G_{RLRL'}^{\text{DMFT/LDA}} \) denotes the LDA+DMFT/LDA-level Green’s function and \( \Sigma(z) \) the self-energy. It is useful to define an auxiliary Green’s function, the path operator \( g_{RLRL'}^\gamma \), as

\[
g_{RLRL'}^\gamma(k,z) = \left[ P_{RL}(z) - S_{RLRL'}^\gamma(k) \right]^{-1},
\]

(11)

which is valid for a general representation \( \gamma \). In Appendix A we present explicit expressions for the potential functions and auxiliary Green’s functions in different representations, as well as their connection to the physical Green’s function. As is apparent in Eq. (11), the full energy- and \( k \)-dependence of the path operator is contained in the potential function and the structure constants, respectively. Furthermore, the potential function is fully local, i.e., it is diagonal in site index. In the following, it will prove convenient to first work in the \( \gamma \)-representation, since here the Green’s function takes a particularly simple form (see Eq. (A2)):

\[
G_{RLRL'}^{\gamma,\text{LDA}}(k,z) = \Delta_{RL}^{-1/2} g_{RLRL'}^\gamma(k,z) \Delta_{RL'}^{-1/2},
\]

(12)

i.e., it is the path operator normalized by the potential parameter \( \Delta_{RI} \). Using Eqs. (12) and (A1), the LDA Green’s function can be evaluated as follows:

\[
[G_{RLRL'}^{\gamma,\text{LDA}}(k,z)]^{-1} = \Delta_{RL}^{1/2} \left[ P_{RI}^{\gamma,\text{LDA}}(z) - S_{RLRL'}^\gamma(k) \right] \Delta_{RL'}^{1/2} = z - C_{RI} - \Delta_{RI}^{1/2} S_{RLRL'}^\gamma(k) \Delta_{RL'}^{1/2}.
\]

(13)

Hence, the LDA+DMFT Green’s function (10) can be written as

\[
[G_{RLRL'}^{\gamma,\text{DMFT}}(k,z)]^{-1} = z - C_{RI} - \Delta_{RI}^{1/2} S_{RLRL'}^\gamma(k) \Delta_{RL'}^{1/2} - \Sigma_{RLRL'}(z),
\]

(14)
i.e., as the resolvent of the Hamiltonian with an embedded self-energy. From Eq. (14), it is obvious that the same result will follow if the potential parameter $C_{RI}$ is replaced by an effective parameter, in which the self-energy is embedded, viz.,

$$C_{RLRL'}^{DMFT}(z) \equiv C_{RI} + \Sigma_{RLRL'}(z).$$

(15)

Hence the effective potential parameter $C_{RLRL'}^{DMFT}$ will now in general be complex, energy-dependent, and have off-diagonal elements. However, $C_{RLRL'}^{DMFT}$ is still local. With this effective potential parameter, the LDA+DMFT level Green’s function can be expressed in a similar form as the LDA-level Green’s function, viz.,

$$[G_{RLRL'}^{DMFT}(k, z)]^{-1} = \Delta_{RLRL'}^{1/2} P_{RLRL'}^{DMFT}(z) - S_{RLRL'}^{\gamma}(k) \Delta_{RLRL'}^{1/2},$$

(16)

where

$$P_{RLRL'}^{DMFT}(z) \equiv P_{RLRL'}^{LDA}(z) - \Delta_{RLRL'}^{1/2} S_{RLRL'}^{\gamma}(z) \Delta_{RLRL'}^{-1/2} = \Delta_{RLRL'}^{1/2} (z - C_{RLRL'}(z)) \Delta_{RLRL'}^{-1/2}.$$  

(17)

Note that due to the self-energy, the effective potential function now has off-diagonal elements.

C. The combined CPA and DMFT loop

For disorder calculations using the CPA, it is more convenient to use the tight-binding $\beta$-representation, since in this case only the potential functions (and not the structure constants) are random. In this case, the representation-dependent potential parameter $V_{\beta}(\text{Eq. } (A4))$ will be modified accordingly:

$$V_{RLRL'}^{\beta,DMFT}(z) = C_{RI} + \Sigma_{RLRL'}(z) - \frac{\Delta_{RI}}{\gamma_{RI} - \beta_{i}}.$$  

(18)

For LDA+DMFT calculations, this form of $V_{RLRL'}^{\beta,DMFT}$ should be used for the potential function $A3$, the path operator $g_{RLRL'}^{\beta,DMFT}$, and the Green’s function $A6$, in order for the Dyson equation to be fulfilled. Note that the transformations in Eqs. (A5) and (A6) are now no longer simply scaled as in the LDA case, but are matrix multiplications due to the presence of off-diagonal terms in the self-energy.

In the following, all quantities will be on the dynamical mean-field level, and we suppress the common superscript “DMFT” for the coherent medium path operators $\tilde{g}_{RLRL'}$, the alloy component path operators $g_{i}$, the coherent potential functions $P_{i}$, and the alloy component potential functions $P_{i}$, which will be defined below. The representation-superscript $\beta$ is kept. An additional superscript $n$ appears to represent the iterative nature of the equations. The superscript $i$ refers to the index enumerating the alloy components at a certain site. We also introduce the concentration of the respective alloy components $i$, at a site $R$, as $c_{i}^{R} (0 \leq c_{i}^{R} \leq 1, \sum_{i} c_{i}^{R} = 1)$. The DMFT impurity problem is solved within the imaginary-axis Matsubara frequency representation, where the Matsubara frequencies are defined as $\omega_{\xi} = (2\xi + 1)i\pi T$, where $\xi = 0, 1, ..., T$ is the temperature. In the following, we use the shorthand $\omega_{\xi} = \{\omega_{0}, ..., \omega_{\xi}, ...\}$ to represent the set of all Matsubara frequencies.

The CPA self-consistency condition requires that the sequential substitution by an impurity atom into an effective, translationally-invariant, coherent medium should produce no further electron scattering, on average. This can be realized by averaging the Green’s function, or, following Györrffy, the path operator:

$$\bar{g}_{RLRL'}^{\beta}(\omega) = \sum_{i} c_{i}^{R} \tilde{g}_{RLRL'}^{i,\beta}(\omega),$$

(19)

where the coherent path operator in the $\beta$-representation,

$$\bar{g}_{RLRL'}^{\beta}(\omega) = \int [\tilde{P}_{RLRL'}^{\beta}(\omega) - S_{RLRL'}^{\gamma}(k)]^{-1} dk,$$

(20)

has been integrated over the Brillouin zone (BZ). In Eq. (20), the coherent potential function $\tilde{P}_{RLRL'}^{\beta}(\omega)$ has been introduced. The alloy component path operators in Eq. (19) are found through a Dyson equation,

$$g_{RLRL'}^{i,\beta}(\omega) = \bar{g}_{RLRL'}^{\beta}(\omega) + \sum_{L'L''} \bar{g}_{RLRL'}^{\beta}(\omega) \times \left[ P_{RLRL'}^{i,\beta}(\omega) - \tilde{P}_{RLRL'}^{\beta}(\omega) \right] g_{RLRL'}^{i,\beta}(\omega).$$

(21)

Here the potentials $P_{RLRL'}^{i,\beta}(\omega)$ are computed according to Eq. (A3), for each type respectively. In order to close the CPA equations self-consistently, a new coherent potential function has to be determined at each iteration. This is done by taking the difference between the inverses of the coherent path operators from the present iteration $n + 1$ and the previous iteration $n$, as follows:

$$\tilde{P}_{RLRL'}^{i,n+1}(\omega) = \tilde{P}_{RLRL'}^{i,n}(\omega) - [\bar{g}_{RLRL'}^{i,n}(\omega)]^{-1} + [\bar{g}_{RLRL'}^{i,n}(\omega)]^{-1}.$$  

(22)

The new coherent potential function can be inserted into Eq. (20), and the cycle can be repeated until self-consistency has been reached. This is performed for each Matsubara frequency $\omega_{\xi}$. Once self-consistency in the CPA equations has been achieved, the Green’s functions for each alloy component can be obtained by normalizing the alloy component path operators in Eq. (21), using the transformation in Eq. (A6). These (local) Green’s functions are then used as input for the DMFT impurity problem, with a separate impurity problem for each alloy component.

The scheme presented above can easily be incorporated within the formalism of the zMTO+DMFT method. Here, the EMTO method (see Appendix B for a brief review) is employed to solve the Kohn-Sham equations for
FIG. 1. Schematic flow diagram of the main DMFT-CPA loop, as implemented within the zMTO+DMFT formalism. Inputs are the alloy component-dependent potential parameters $C$, $\Delta$ and $\gamma$, taken from a LDA-level self-consistent EMTO-CPA calculation. For each Matsubara frequency along the imaginary energy axis, the CPA equations are solved self-consistently. The alloy impurity Green’s functions are supplied to the DMFT impurity problem, which is solved self-consistently, giving the self-energies as output. These self-energies modify the potential parameters, and both the CPA and DMFT equations are solved together self-consistently. To make the scheme charge self-consistent, the change in the density due to correlation, $\Delta n(r)$, can be added to the EMTO-CPA charge density $n(r)$, and then the Kohn-Sham equations are iterated until convergence.

random alloys self-consistently, within the CPA, on the level of the LDA. The DMFT impurity problem is then solved in the Matsubara representation, using linearization techniques to evaluate the alloy components Green’s functions, as presented above. This can be done both on the LDA-level (setting $\Sigma = 0$) and on the DMFT-level (using the self-energy from the DMFT impurity problem). The charge self-consistency is achieved similarly as in Ref. [34], by computing moments of the alloy component Green’s function at LDA and DMFT level. The difference between the charge densities computed in this way can then be added as a correction on the LDA-level charge computed within the EMTO method. In Figure 1, we present a schematic picture of the self-consistent loops.

IV. RESULTS

In order to demonstrate the feasibility of our proposed method, we apply it to investigate the electronic structure of the binary Cu$_{1-x}$Pd$_x$ alloy and the semi-Heusler compound NiMnSb, with partially exchanged Ni and Mn components.

A. Computational details

In all calculations, the kink cancellation condition was set up for 16 energy points distributed around a semi-circular contour with a diameter of 1 Ry, enclosing the valence band. The BZ integrations were carried out on an equidistant $13 \times 13 \times 13$ k-point mesh in the fcc BZ. For the exchange-correlation potential the local spin density approximation with the Perdew-Wang parameterization was used. To solve the DMFT equations, we used the spin-polarized $T$-matrix fluctuation-exchange (SPT-FLEX) solver. In this solver, the electron-electron interaction term can be considered in a full spin and orbital rotationally invariant form. Since specific correlation effects are already included in the exchange-correlation functional, so-called “double counted” terms must be subtracted. To achieve this, we replace $\Sigma(E)$ with $\Sigma(E) - \Sigma(0)$ in all equations of the DMFT procedure. Physically, this is related to the fact that DMFT only adds dynamical correlations to the DFT result. The Matsubara frequencies were truncated after $\xi = 1024$ frequencies, and the temperature was set to $T = 400$ K. The values for the Coulomb $U$ and the exchange $J$ parameters are discussed in connection with the presentation of the results in each case. The densities of state were computed along a horizontal contour shifted away from the real energy axis. At the end of the self-consistent calculations, to obtain the self-energy on the horizontal contour, $\Sigma(\omega)$ was analytically continued by a Padé approximant. For the studied alloys a $spd$-basis was used. For the Cu-Pd system, the Cu 4$s$ and 3$d$ states, and for Pd the 5$s$ and 4$d$ states, were treated as valence. For the case of NiMnSb, the Ni and Mn 4$s$ and 3$d$ states, and for Sb the 5$s$ and 5$p$ states, were treated as valence. The core electron levels were computed within the frozen-core approximation, and were treated fully-relativistically. The valence electrons were treated within the scalar-relativistic approximation. Af-
fter self-consistency was achieved for NiMnSb, the density of states (DOS) was evaluated with a 21 × 21 × 21 k-point mesh, in order to get an accurate band gap.

B. Spectral functions and the Fermi surface of Cu₁₋ₓPdₓ random alloys

Discrepancies between the measured photoemission spectra and the KKR-CPA spectral functions for various Cu-Pd alloys were often discussed in the literature. In particular LDA-CPA results for the Pd partial DOS of the Cu₀.₇₅Pd₀.₂₅ alloy reveal a three-peak structure (black line, Figure 2) peaks marked by A, B, and C), similar to the DOS of pure fcc-Pd. Experimental data on the other hand, see also inset of Figure 2, show a contracted band width for the partial DOS and do not resolve the peak at the bottom of the band (marked by C). A detailed discussion concerning these discrepancies can be found in Ref. [52]. We note that the frequently discussed reasons for these discrepancies are connected to matrix element effects, broadening by electronic self-energy, and local lattice distortions, that go beyond the capabilities of standard CPA. Although it is not our intention to address all of the above inconsistencies, our current implementation allows us to address the possible source of discrepancy in connection to the combined disorder and correlation effects.

![FIG. 2. Partial density of states of Pd in the Cu₀.₇₅Pd₀.₂₅ alloy, as a function of Coulomb interaction U. Inset: Experimental photoemission data taken from Ref. [53].](image)

We have previously investigated the electronic structure of fcc-Pd within the framework of the LDA+DMFT method using the perturbative FLEX impurity solver. Recently, the properties of fcc-Pd were revisited using a lattice (non-local) FLEX solver. These recent calculations support our results using the local approximation of the self-energy. Consequently, we study the electronic correlations in the CuPd alloys using the same local DMFT technique as we used before. In particular we consider modeling correlations only for the Pd alloy component.

![FIG. 3. (a) Fermi surface (Bloch spectral function) for the Cu₀.₆₀Pd₀.₄₀ alloy with U=4 eV. (b) Difference of spectra between U = 4 eV and U = 0. The color maps indicate the spectral weight in arbitrary units.](image)

In Figure 2, we present the spectral function (DOS) for the Cu₀.₇₅Pd₀.₂₅ alloy, as a function of the Coulomb parameter U. All curves were evaluated at the lattice constant given by a linear interpolation between that of pure Cu and pure Pd (Vegard’s law), which in this case corresponds to a = 3.68 Å. Vegard’s law has previously been shown to hold in a larger range of concentrations for Cu-Pd within KKR-CPA. As the Coulomb interaction is increased, the peak close to the bottom of the band (C) shifts towards the Fermi energy, while the major peak close to E_F (A) remains unchanged. The high binding energy peak (C) loses intensity with increasing U, and the spectral weight is shifted to higher binding energy, where it builds up a satellite structure (not shown). A similar behavior in the spectral weight shift was also found for pure Pd. The results of the calculations including self-energy effects shown in Figure 2 bring the spectral function more in line with experimental photoemission data (see also inset). Since we neglect matrix element effects due to the photoemission process, as well as local lattice relaxations, we do not make a quantitative statement concerning the differences between theory and experiment. However, our calculation shows that the proposed method which combines correlation and alloy disorder effects, provides the correct trend in the spectral function.

In the following we comment upon the disorder and correlation induced modifications in the shape of the Fermi surface of CuPd alloys. On the basis of KKR-CPA calculations Györffy and Stocks proposed an electronic mechanism which determines short-range order effects...
FIG. 4. (a) Spin-resolved spectral function around the Fermi level for NiMnSb with Mn-Ni interchange, from 0% (no disorder, light blue solid line) to 0.1% (dark blue dashed line), 0.5% (green dash-dotted line). The red solid line corresponds to \( U = 0 \) and no disorder. (b) Same as in (a), but for the larger degrees of disorder 1% (dark blue dashed line), and 5% (green dash-dotted line).

experimentally seen in CuPd alloys. The experimental observation, namely the dependence of the scattering intensities on concentration in these alloys, was traced back to the flattening of the Fermi surface sheets with increasing Pd concentration. According to their results, the Fermi surface must change from a convex shape in the Cu-rich alloy to a concave one for the Pd-rich limit, in a continuous fashion. Consequently the Fermi surface is forced to be almost flat for some concentration, giving rise to nesting phenomena. This was later confirmed by further experiments and CPA calculations.

According to previous calculations, a flattened Fermi surface in the \( \Gamma X K \) plane was obtained for the Cu\(_{0.60}\)Pd\(_{0.40}\) alloy. In Figure 3(a) we plot our results for the Fermi surface of the same alloy. In our calculations we used for the lattice constant the value \( a = 3.72 \) Å (from Vegard’s law), and electronic interactions on the Pd alloy component were parameterized by \( U = 4 \) eV, and \( J = 1.2 \) eV. The Fermi surface is represented in the (010) and (110) planes of the fcc BZ. The major part of the Fermi surface consists of the electron sheet centered at the \( \Gamma \)-point. This sheet goes from convex to concave with Pd-alloying, forcing parts of the sheet to be nearly flat at 40% Pd. Our result is in good agreement with previous KKR-CPA calculations. To quantify the effect of correlation, we plot in Figure 3(b) the difference between the correlated (\( U = 4 \) eV) and the non-correlated (\( U = 0 \)) case. Note the relatively small scale, which shows that the Fermi surface is insensitive to correlation effects.

C. Interplay of correlation and disorder in Mn-Ni partially interchanged NiMnSb

Half-metallic ferromagnets (HMF) are ferromagnetic systems which are metallic in one spin channel, while for the opposite spin direction the Fermi level is situated in a gap. Such systems would therefore present a full spin-polarization at the Fermi level, and have consequently drawn considerable interest due to their potential application in spintronics. One of the first systems to be characterized as a HMF is the semi-Heusler NiMnSb. The crystal structure of the NiMnSb compound is cubic with the space group \( F \bar{4}3m \) (No. 216). It consists of four interpenetrating fcc sublattices equally spaced along the [111] direction. The Ni lattice sites are situated at \((0,0,0)\), Mn sites are at \((1/4,1/4,1/4)\), and Sb is situated at \((3/4,3/4,3/4)\). The position at \((1/2,1/2,1/2)\) is unoccupied in the ordered alloy. In experiment, contrary to the DFT prediction, the measured spin-polarization of NiMnSb is only 58\%\(^{61}\). Several suggestions have been given to explain this large reduction in spin-polarization. Among them we mention electronic correlation effects\(^{62,63}\) and disorder\(^{64,65}\).

Within the current implementation we have the opportunity to study the combined effect at equal footing. In the present calculations we use the experimental lattice constant, \( a = 5.927 \) Å. To parametrize the Coulomb interaction the values \( U = 3 \) eV and \( J = 0.8 \) eV was used, which are in the range of previous studies.\(^{66-74}\) Only the Mn \( d \) states were treated as correlated. Because the Ni \( 3d \) bands in NiMnSb are almost filled, these are subject to minor correlation effects, as shown previously.\(^{72}\)

The effect of electronic correlations is the appearance of nonquasiparticle (NQP) states in the minority spin gap (spin down channel) just above the Fermi level. The origin of these many-body NQP states is connected with
“spin-polaron” processes: the spin-down low-energy electron excitations, which are forbidden for the HMF in the one-particle picture, turn out to be allowed as superpositions of spin-up electron excitations and virtual magnons. By direct computation, spin-orbit effects were found to be negligible in NiMnSb. A partially filled minority spin gap was obtained but the material remains essentially half-metallic with a polarization of the DOS of about 99%. The interplay of spin-orbit induced states and NQP states have been also discussed. In contrast with the spin-orbit coupling, correlation induced NQP states have a large asymmetric spectral weight in the minority-spin channel, leading to a peculiar finite-temperature spin depolarization effect. It has been shown that also disorder induces minority-spin states in the energy gap of the ordered material. These states widen with increasing disorder. This behavior leads to a reduced minority-spin band gap and a displacement of the Fermi energy within the original band gap.

The current implementation gives us the opportunity to investigate the possible interplay of disorder-induced and NQP states. To this end we perform electronic structure calculations considering the partial interchange of Ni and Mn, (Ni1−xMnx)(Mn1−xNi2)Sb, which leaves the overall stoichiometry and number of electrons constant. In Figure 4, we show the total DOS around the Fermi level for a number of different disorder levels. In the Figure 4(a)/(b) the LDA+DMFT DOS for smaller degrees of disorder $x = 0.1, 0.5$% and respectively for larger disorder $x = 1, 5$% is seen. The results for the clean, $x = 0$% (ideal) case, NiMnSb, are presented with read lines (non-interacting, $U = 0$), and light blue (DMFT). The minority spin gap is about 0.5 eV wide and is formed between the occupied Ni $d$, Sb $p$ and Mn $t_{2g}$ states. In the majority spin channel (spin up), Mn $d$ states dominate at $E_F$. Already at 0.1% disorder (dark blue dashed line) minority states appear below $E_F$. These states are generated by the presence of Ni impurities at the Mn site, as previously shown by Orgassa et al. Furthermore, the upper band edge is shifted to higher energy. As the disorder is increased, the width of the Ni impurity states are increased. With correlation, minority spin states appear just above the Fermi level. These NQP states arise from many-body electron-magnon interactions. At larger degrees of disorder, see Figure 4(b), the impurity states and the NQP states overlap in energy, removing the spin-down gap. Hence, the combination of exchange disorder and correlation effects removes the half-metallic state in NiMnSb.

Figure 5(a)/(b) displays the self-energy along the real energy axis for the Mn $t_{2g}/e_g$ states, respectively, for a Mn-Ni interchange of 5%. The blue lines correspond to the Mn at the Mn-site, and is similar to the self-energy for the pure NiMnSb (not shown). The self-energy behaves as in previous calculations, namely: The spin-down channel (blue down-triangles) has a self-energy that is fairly small below $E_F$, but starts to increase above $E_F$. At around 0.5 eV above $E_F$, the self-energy shows a hump, which gives rise to the NQP peak in the spectral function. The spin-up channel self-energy (blue up-triangles) behaves differently, it is relatively large below $E_F$, while being small in magnitude above $E_F$. The self-energy for the impurity Mn, situated at the Ni-site, is marked by the red lines in Figure 5(a)/(b). It is interesting to note that the trend seen for the spin channels has the reversed behavior compared to the self-energy on the Mn-site. For the spin-down channel (red down-triangle), the self-energy is large below $E_F$, while it is small above $E_F$. The trend is opposite for the spin-up channel (red up-triangle). This reversal of behavior be-
between the Mn-site self-energy and the Ni-site self-energy can be understood by looking at the magnetic moments in the system. In pure NiMnSb, the total magnetic moment is (integer) \(4 \mu_B\), with the main contribution stemming from the Mn-site \((\sim 3.8 \mu_B)\). As the pure system starts to be disordered, a Mn-moment of opposite sign \((\sim -2 \mu_B)\), depending on the interchange concentration) develops at the Ni-site. Hence, the moment of the impurity Mn on the Ni-site aligns antiferromagnetically with the Mn moment on the Mn-site.

It is of interest to investigate how the effect of disorder, i.e., the degree of Mn-Ni interchange, influence the formation of NQP states. For this reason, in the inset of Figure 5(b), we plot the Mn-site self-energies of the dominant \(e_g\) orbitals for different disorder concentrations. For minor degrees of Mn-Ni interchange (up to 5%), the sudden increase in \(\text{Im } \Sigma(E)\) just above \(E_F\) (dashed blue lines of Figure 5), signaling the departure from Fermi liquid behavior, remains unaffected. It should also be noted that the Ni-site self-energy (Figure 5, red lines), follows the Fermi liquid (quasiparticle) behavior \(\text{Im } \Sigma(E) \propto (E - E_F)^2\). The Ni \(d\) band in NiMnSb is almost fully occupied, leaving little possibility for magnons to be excited, therefore weak electron-magnon interaction exists in the Ni-sublattice and no NQP states are visible in the density of states.

V. CONCLUSION AND OUTLOOK

In this paper we developed a calculation scheme within the framework of the density functional theory, which allows one to study properties of disordered alloys including electronic correlation effects. We model disorder using the coherent potential approximation and include local but dynamic correlations through dynamical mean field theory. Similar to our previous implementation\(^{[34]}\) the DFT-LDA Green’s function is computed directly on the Matsubara contour. Simultaneously the CPA is implemented within the LMTO formalism also in the Matsubara representation. Within the LMTO formalism the CPA effective medium is naturally encoded in the potential function, which alone contains the necessary information about the atomic configuration (assuming that a suitable screening representation is chosen). As shown in this paper, the simple parameterization of the potential function allows us to easily embed the self-energy into the standard LMTO potential parameters. Accordingly, the previously developed CPA schemes within the various muffin-tin approximations can then be used with only minor changes.

We presented results of the electronic structure calculation for two disordered alloys: the \(\text{Cu}_3\text{Pd}_x\) system, and the half-metallic NiMnSb semi-Heusler, in which correlations were considered for Pd and Mn alloy components respectively. For the case of the binary \(\text{CuPd}\) system, we see that the inclusion of electronic correlation improves the agreement with the experimental spectral functions for \(x = 0.25\). For a Pd concentration of \(x = 0.4\) the Fermi surface, which is well captured already on the level of the LDA, remains more or less unchanged as correlation effects are turned on. In the second example, the partial exchange of Mn and Ni in NiMnSb was investigated, simultaneously with correlation effects. Already for low levels of disorder, impurity states appear below the Fermi level, while many-body induced nonquasiparticle states appear just above the Fermi level. Both these states contribute to the closing of the minority-spin gap.

In the future, the present method will be extended to compute total energies within the full-charge density technique\(^{[39]}\) making it possible to study the energetics of anisotropic lattice distortions\(^{[20]}\) in alloys. Another interesting venue is to change the arithmetic configuration average used in the CPA to the geometric average used in typical medium methods\(^{[27]}\). This will allow one to investigate the effects of Anderson localization\(^{[10]}\) in realistic materials.

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Appendix A: Relations and formulas within the LMTO method

Within the nearly-orthogonal \(\gamma\)-representation, the potential function takes the simple form

\[
P_{Rl}(z) = \frac{z - C_{Rl}}{\Delta_{Rl}}. \tag{A1}\]

An insertion of this form into Eq. (11), and comparing with Eq. (9), one sees that

\[
g_{RL'RL'}^\gamma(k, z) = \sqrt{\Delta_{Rl}G_{RLRL'}^\gamma(k, z)\Delta_{RL'}}. \tag{A2}\]

i.e., the Green’s function is the normalized path operator.

In the case of a random alloy, the potential parameters \(C_{Rl}, \Delta_{Rl}\) and \(\gamma_{Rl}\) will be site-dependent random parameters. Hence, both the potential function \(P_{Rl}(z)\), Eq. (A1), and the structure constants \(S^\gamma\), will be random
within the γ-representation. To avoid this, it is useful to switch to the tight-binding β-representation, as has been pointed out previously. Within the tight-binding β-representation, the potential function takes the form

\[ P_{\beta}^p(z) = \frac{\Gamma_{\beta}}{V_{\beta}^z - z} + \frac{1}{\gamma_{\beta} - \beta}, \]  

(A3)

where here the representation-dependent potential parameters \( V_{\beta} \) and \( \Gamma_{\beta} \) are given by

\[ V_{\beta} = C_{\beta} - \frac{\Delta_{\beta}}{\gamma_{\beta} - \beta}, \quad \Gamma_{\beta} = \frac{\Delta_{\beta}}{(\gamma_{\beta} - \beta)^2}. \]  

(A4)

The β-parameters can be found tabulated in several sources. The structure constants \( \beta \) depend only on the geometry of the underlying lattice, and only the potential function \( P_{\beta} \) is random. The path operator in the β-representation, \( g_{RLR}^\beta(k,z) \), is given similarly as in Eq. (11). The following relation allows to transform path operators between different representations:

\[ g^\beta(z) = (\beta - \gamma) \frac{P^\gamma(z)}{P^\beta(z)} + \frac{P^\gamma(z)}{P^\beta(z)} g^\gamma(z) \frac{P^\gamma(z)}{P^\beta(z)}. \]  

(A5)

where we have omitted the indices for simplicity. Using this transformation, and Eqs. (A1), (A3), and (A2), the Green’s function can be obtained from \( g_{RLR}^\beta(k,z) \):

\[ G_{RLR}^\beta(k,z) = \frac{1}{z - V_{RL}^\beta} + \sqrt{\frac{\Gamma_{RL}^\beta}{\gamma_{RL}^\beta}} g_{RLR}^\beta(k,z) \frac{\sqrt{\Gamma_{RL}^\beta}}{z - V_{RL}^\beta}, \]  

(A6)

Note that the transformations in Eqs. (A5) and (A6) are simply energy-dependent scalings of the path operator, since the potential parameters and the potential functions are diagonal matrices.

We here briefly mention the accuracy of the presented expressions. The formulas as written above give correct energies up to second order in \((\epsilon - \epsilon_k)\). A way to improve on this is by a variational procedure, which produces a new Hamiltonian, giving eigenvalues correct to third order. Correspondingly, the substitution \( z \rightarrow z + (z - \epsilon_k)^2 p \) in Eq. (A6) gives a third-order expression for the potential function. Here, \( p = \langle \phi^p | \phi^p \rangle \) is a (relatively small) potential parameter. In order to compare the spectra arising from the different orders of LMT0’s, we investigated the DOS for various systems using either second or third order potential functions, and comparing the result with the DOS computed from the Hamiltonian through the spectral representation. We found that while at second order there was no difference between the DOS, for third order there were clear differences between the spectra. This can be attributed to the false poles present in the third-order potential function, since the energy dependence is now not linear, but cubic. In practice, we found that this lead to a loss of spectral weight in the Green’s function of Eq. (A6), compared to the spectral representation. Hence, we in this paper only consider second order potential functions in Eq. (A6).

Appendix B: Exact Muffin-Tin Orbitals method

One choice of basis for the solution of the Kohn-Sham equation is the energy-dependent exact muffin-tin orbitals. They are constructed as a sum of the so called partial waves, the solutions of the radial equations within the spherical muffin-tins, and of the solutions in the interstitial region. Using this basis, the Kohn-Sham eigenfunctions can be expressed as

\[ \Psi_j(r) = \sum_{RL} \tilde{\psi}_{RL}(\epsilon_j, r_R) \phi_{RL,j}^a, \]  

(B1)

where the superscript \( a \) denotes the screening representation used in the EMTO theory.

The expansion coefficients, \( \phi_{RL,j}^a \), are determined so that the \( \tilde{\psi}_{RL}(\epsilon_j, r_R) \) is a continuous and differentiable solution of Eq. (11) in all space. This leads to an energy-dependent secular equation, \( K_{RLR}^a(\epsilon_j) \phi_{RL,j}^a = 0 \), where \( K_{RLR}^a \) is the so called kink matrix, viz.

\[ K_{RLR}^a(\epsilon_j) \phi_{RL,j}^a = \alpha \delta_{RL} \delta_{LL} D_{RL}^a(\epsilon_j) - a S_{RL}^a(\epsilon_j) \phi_{RL,j}^a = 0, \]  

(B2)

\( D_{RL}(\epsilon_j) \) denotes the EMTO logarithmic derivative function, and \( S_{RL}^a(\epsilon_j) \) is the slope matrix. The energy dependence of the kink matrix and the secular equation poses no difficulties, since the DFT problem can be solved by Green’s function techniques (see, for example, Ref. 80). By defining the path operator \( g_{RLR}^a(k,z) \) as the inverse of the kink matrix,

\[ \sum_{RL} K_{RLR}^a(\epsilon_j) \phi_{RL,j}^a g_{RLR}^a(k,z) = \delta_{RL} \delta_{LL} D_{RL}^a(\epsilon_j) - a S_{RL}^a(\epsilon_j) \phi_{RL,j}^a, \]  

(B3)

the poles of the path operator in the complex energy plane will correspond to the eigenvalues of the system. The energy derivative of the kink matrix, \( K_{RLR}^a(\epsilon_j) \), gives the overlap matrix for the EMTO basis set, and hence it can be used to normalize the path operator \( g_{RLR}^a(\epsilon_j) \), which gives the EMTO Green’s function:

\[ G_{RLR}(k,\epsilon_j) = \sum_{RL} g_{RLR}(k,\epsilon_j) K_{RLR}^a(\epsilon_j) \phi_{RL,j}^a, \]  

(B4)

where \( I_{RL}(\epsilon_j) \) accounts for the unphysical poles of \( K_{RLR}^a(\epsilon_j) \). The use of Green’s functions also facilitates the implementation of the CPA, the reader is referred to Refs. 17, 18 and 20 for more detailed discussions.
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93. B. L. Gyorgy and G. M. Stocks, Phys. Rev. Lett. 50, 374 (1983).

94. E. Bruno, B. Ginatempo, and E. S. Giuliano, Phys. Rev. B 63, 174107 (2001).

95. M. I. Katsnelson, V. Y. Irkhin, L. Chioncel, A. I. Lichtenstein, and R. A. de Groot, Rev. Mod. Phys. 80, 315 (2008).

96. R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. 50, 2024 (1983).

97. R. J. Soulen, J. M. Byers, M. S. Ososky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. Tanaka, J. Nowak, J. S. Moodera, A. Barry, and J. M. D. Coey, Science 282, 85 (1998).

98. L. Chioncel, M. I. Katsnelson, R. A. de Groot, and A. I. Lichtenstein, Phys. Rev. B 68, 144425 (2003).

99. D. Orgassa, H. Fujiwara, T. C. Schulthess, and W. H. Butler, Phys. Rev. B 60, 13237 (1999).

100. J. J. Attema, C. M. Fang, L. Chioncel, G. A. de Wijs, A. I. Lichtenstein, and R. A. de Groot, J. Phys.: Condens. Matter 16, S5517 (2004).

101. M. Ekholm, P. Larsson, B. Alling, U. Helmersson, and I. A. Abrikosov, Journal of Applied Physics 108, 093712 (2010).

102. C. Morari, W. H. Appelt, A. Östlin, A. Prinz-Zwick, U. Schwingenschlögl, U. Eckern, and L. Chioncel, Phys. Rev. B 96, 205137 (2017).

103. D. M. Edwards and J. A. Hertz, Journal of Physics F-Metal Physics 3, 2191 (1973).

104. P. Mavropoulos, K. Sato, R. Zeller, P. H. Dederichs, V. Popescu, and H. Ebert, Phys. Rev. B 69, 054424 (2004).

105. L. Chioncel, E. Arrigoni, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. Lett. 96, 137203 (2006).

106. H. Terletska, Y. Zhang, L. Chioncel, D. Vollhardt, and M. Jarrell, Phys. Rev. B 95, 134204 (2017).

107. H. L. Skriver and N. M. Rosengaard, Phys. Rev. B 43, 9538 (1991).

108. O. K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. B 34, 5253 (1986).

109. O. K. Andersen, T. Saha-Dasgupta, R. W. Tank, C. Arcangeli, O. Jepsen, and G. Krier, in Electronic Structure and Physical Properties of Solids, edited by H. Dreyssé (Springer Verlag, Berlin Heidelberg, 1999) pp. 3–84.

110. R. Zeller, J. Deutz, and P. Dederichs, Solid State Communications 44, 993997 (1982).