Disorder in materials with complex crystal structures: the Non-Local Coherent Potential Approximation for compounds with multiple sublattices

A Marmodoro and J B Staunton
Department of Physics, University of Warwick, Coventry CV4 7AL, UK
E-mail: A.Marmodoro@warwick.ac.uk

Abstract. Over the last few years the Non-Local Coherent Potential Approximation (NL-CPA) has been shown to provide an effective way to describe the electronic structure and related properties of disordered systems, where short-range order (SRO) and other local environment effects are important. Here we present its generalization to materials with multi-atom per unit cell lattices. The method is described using a Green function formalism and illustrated by an implementation for a simplified one-dimensional tight-binding model with substitutional disorder. This development paves the way for a natural reimplementation of the Korringa-Kohn-Rostoker (KKR) multiple scattering solution of Kohn-Sham equations for ab-initio calculations of real materials.

1. Introduction
A certain degree of disorder is a common feature in all real materials, and may have a very significant impact on their electronic structure and related properties. With the loss of translational invariance an analytical, exact solution becomes rapidly inaccessible even for simplified, small size model systems, and the typical challenges of a fully ab-initio density functional theory -based approach are also strongly enhanced.

The Coherent Potential Approximation (CPA) [1] has historically provided a powerful, fully self-consistent mean field approximation framework for the systematic evaluation of local disorder effects across a wide variety of solid state physics applications. In combination with the Korringa-Kohn-Rostoker multiple scattering method for solving the electronic problem of the Kohn-Sham equations [2,3] it is possible to fully account for the impact of on-site deviations from periodicity. Bloch states, on the average, are correctly predicted to acquire a finite lifetime, and the conceptual tool of the Bloch spectral function is used to generalize the original band structure description in the presence of randomly distributed impurities.

A recent development of the method (NL-CPA) [4, 5, 6, 7, 8, 9] has enhanced its capabilities to also cover the effective evaluation of off-diagonal disorder necessary for an accurate treatment of short-range order (SRO) effects or dopant clustering, at a comparatively negligible computational cost with respect to similarly accurate supercell -based calculations [10, 11, 12].
This extension is based on a reinterpretation of the original CPA self-consistency conditions as the first order term only in a coupled expansion over a coarse grained set of $N_c \geq 1$ sites $R_I$ and associated discrete cluster momenta $K_n$, in reciprocal space \[4\]. These are selected to preserve the original point group symmetries of the underlying geometry \[13\], and have so far allowed successful investigations at a higher than single-site resolution of a range of simple crystal structures derived from a cubic lattice (\textit{Strukturbericht} designation $A_h$, $A_1$, $A_2$), with application to metallic alloys \[5\],\[14\] and electrical conductivity studies \[9\],\[15\] where macroscopic observables are found to be strongly affected by local environment effects and formation of complexes.

On the other hand, the problem of how to handle the associated Brillouin zone coarsening for a system with many atom per unit cell has so far made the idea incompatible with an earlier development, designed to address multi-sublattice systems (MS-CPA) \[16\]. In such an approach the same original limitations of a local-only single site approximation still persist, but it is possible to investigate a broad range of selective chemical disorder scenarios, such as hydrogen absorption for energy storage\[17\], cation defects in transition metal oxides \[18\], as well as cases where the local order parameter may be for instance represented by the orientation of a local moment in a magnet\[19\],\[20\] or by strain and polarization in a ferroelectric \[21\].

We propose here an unification of the two extensions (MS-NL-CPA) to combine their respective merits for the efficient treatment of disorder and SRO effects in arbitrary complex structures. In order to aid the interpretation of investigations for the first real materials from an ab-initio DFT-KKR adaption, for which preliminary calculations are currently under evaluation, we present here the general method in a flexible Green function formalism and illustrate for better clarity the type of physics it can describe by an implementation for a tight-binding (TB) model for substitutional disorder.

The setup of this simplified, 1D representation of the problem is introduced in section 2. The new general formalism and a practical algorithm for its numerical solution are described in section 3. Results from this new framework are first checked in the special test case of a degenerate complex unit cell system, in which the NL-CPA treatment for a single atom per unit cell approach can be recovered from the MS-NL-CPA (section 4.1). We then discuss a selection of representative instances of the full model, illustrating the topical examples of selective doping with SRO, and order-disorder transitions (sections 4.2.1, 4.2.2). The final section draws some overall conclusions including implications for studies of realistic systems.

2. Model description and Green function solution

A basic model for the problem of substitutional disorder in a complex unit cell scenario can be given by the tight-binding hamiltonian:

$$H = \sum_{i,j} \sum_{s,s'} H_{(i,s);(j,s')} H_{(i,s);(j,s')} = W_{(i,s);(j,s')} + \epsilon_{(i,s)} \delta_{i,j} \delta_{s,s'},$$  \hspace{1cm} (1)

where the general $i, j$ indices refer to the $N \to \infty$ superlattice vectors of an effectively infinite disordered sample, and the $s, s' = 1, \ldots, N_{\text{sub}}$ indices identify different sublattices within a complex unit cell of $N_{\text{sub}}$ atomic sites.

In our 1D TB model we restrict kinetic effects to nearest neighbour hopping processes in the form:

$$W_{(i,s);(j,s')} = t \delta_{s,s'=s+1} \delta_{ij} + t \delta_{i,j=1} \left( \delta_{s,1} \delta_{s'=N_{\text{sub}}} + \delta_{s'=1} \delta_{s,N_{\text{sub}}} \right)$$ \hspace{1cm} (2)

\begin{align*}
\text{intra-cell hopping} & \quad \text{inter-cell hopping} \\
\end{align*}
where the positive hopping parameter \( t \) describes lowering of total energy through electronic delocalization among equidistant ions.

Local substitutions are represented by the second term \( \epsilon_{(i,s)} \), which in a general treatment may acquire different values among \( N_{\text{alt},s} \) alternative ones, selected from the species available to each specific sublattice \( s \). Alternatively, the method can also be appropriate to systems with off-diagonal disorder, involving instead different site to site hopping parameters.

In this illustrative 1D example unit cells are repeated at \(|R_i - R_j| = 0, L, 2L, \ldots\), with periodic boundary conditions, and we make the further convenience-only assumption of equal separation between the \( N_{\text{sub}} \) sublattices at \(|a_s - a_{s'}| = 0, a, 2a, \ldots, (N_{\text{sub}} - 1)a\), with \( L = N_{\text{sub}} a \) (figure 1). We apply this description to the example of a \( N_{\text{sub}} = 2 \) unit cell binary compound of the form: \((A_{c1}B_{1-c1})(C_{c2}D_{1-c2})\).

**Figure 1.** Schematic illustration of a 1D tight-binding model for substitutional disorder in a complex unit cell, here evaluated under periodic boundary conditions for \( N_{\text{sub}} = 2, L = 2a \).

An exact solution to the model of eq. 1 would in principle require accurate knowledge of the atomic species on each site of the effectively infinite \( N \) unit cells in the bulk, and the ability to numerically handle the associated \((N \times N_{\text{sub}}) \times (N \times N_{\text{sub}})\), almost tridiagonal sparse matrix \( H \):

\[
H = \begin{pmatrix}
\epsilon_{(1,1)} & -t & 0 & \ldots & -t \\
-t & \epsilon_{(1,2)} & -t & \ldots & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots \\
-t & \ldots & \ldots & -t & \epsilon_{(N,N_{\text{sub}})}
\end{pmatrix}
\]

(3)

to construct the direct space Green function \[22\]:

\[
(zI - H) \mathcal{G}(z) = I \text{ evaluated at the complex energy: } z = \epsilon + i\eta
\]

(4)

Considering however that self-averaging effects over a great number of possible configurations will always dominate actual measurements even in a microscopic sample, we can resort instead to an effective medium description. Translational invariance is reintroduced as an *a priori* condition, following the motivations of the original CPA development. With the definition of a mean-field self-energy \( \Xi \), it is then possible to directly compute the bulk-averaged Green function \( \langle \mathcal{G}(z) \rangle \) as:

\[
\langle \mathcal{G}(z) \rangle = \langle (z - H)^{-1} \rangle = \langle z - W - \Xi(z) \rangle^{-1}
\]

(5)

from which observables such as the density of states (DOS) can be immediately determined:

\[
n(\epsilon) = \sum_{s=1}^{N_{\text{sub}}} n_s(\epsilon) \quad \text{with sublattice contributions:} \quad n_s(\epsilon) = \lim_{\eta \to 0^+} -\frac{1}{N\pi} \text{Im} \sum_{i=1}^{N} \langle \mathcal{G}_{(i,s);(i,s'=s)}(z) \rangle
\]

(6)
The problem is therefore transformed into the search for a properly sublattice-resolved self-energy \( \Xi \). This shall in particular apply to the general case \( N_{\text{sub}} \geq 1 \), and keep track of possible SRO correlations at multiple length scales beyond a single site \( N_c = 1 \) CPA description, recovering the exact solution in the limit \( N_c \rightarrow N \).

3. The Multi-Sublattice generalization of the NL-CPA

We follow and generalize the derivation of the single atom per unit cell NL-CPA as provided by Jarrell and Krishnamurthy \[13\] and Rowlands et al. \[4\]. With the introduction of translational invariance at the effective medium level, averaged quantities must be periodic at the appropriate length scales across every complex unit cell, but retain sublattice dependence. This condition can be enforced by introducing a (super)lattice Fourier transform \( \hat{G} \) satisfying the idempotence relationship:

\[
\frac{1}{N_c} \sum_{K_n} e^{iK_n \cdot (R_I - R_J)} = \delta_{I,J}
\]

for \( K_n, R_I, R_J \) general vectors identifying different coarse-graining regions respectively in reciprocal and direct space \[4\], to express the self-energy as:

\[
\Xi_{s,s'}(K_n, z) = \sum_{J=1}^{N_c} \Xi_{(I,s);(J,s')}(z) e^{-iK_n \cdot (R_I + a_s - R_J - a_{s'})}
\]

\[
(8a)
\]

\[
\Xi_{(I,s);(J,s')}(z) = \frac{1}{N_c} \sum_{K_n} \Xi_{s,s'}(K_n, z) e^{iK_n \cdot (R_I + a_s - R_J - a_{s'})}.
\]

(8b)

Correspondingly, the bulk-averaged Green function of eq. 5 is:

\[
\mathcal{G}_{(I,s);(J,s')}(z) = \sum_{J=1}^{N_c} \mathcal{G}_{s,s'}(K_n, z) e^{iK_n \cdot (R_I + a_s - R_J - a_{s'})}
\]

(9)

with:

\[
\mathcal{G}_{s,s'}(K_n, z) = \frac{N_c}{\Omega} \int_{\Omega K_n} [z \nabla - W(k) - \Xi(K_n, z)]_{s,s'}^{-1} dk
\]

(10)

where the integration extends over the original Brillouin zone \( \Omega \), without the reciprocal space rescaling that would be involved in a supercell-based description of the problem \[4\]. The Brillouin zone of the lattice is instead partitioned into \( N_c \) equal “tiles” \( \Omega K_n \) of extension \( \Omega / N_c \), centered on each cluster momentum \( K_n \) \[4\], to give the solution \( \mathcal{G}_{s,s'}(K_n, z) \) as a coarse-grained approximation of the implicit equation:

\[
\mathcal{G}_{s,s'}(k, z) = \mathcal{G}_{s,s'}^0(k, z) + \sum_{n_1,n_2} \mathcal{G}_{s_1,s_2}^0(k, z) \Xi_{s_1,s_2}(k, z) \mathcal{G}_{s_2,s'}(k, z)
\]

(11)

for \( \mathcal{G}_{s,s'}^0(k, z) = (z - W_{s,s'}(k))^{-1} \) the free space propagator, and \( k \) the originally continuous momentum defined for \( N \rightarrow \infty \) within the whole \( \Omega \).

Furthermore by introducing in direct space a cavity Green function

\[
\mathcal{G}_{(I,s);(J,s')\text{ cav}}(z) = (\mathcal{G}_c^{-1}(z) + \Xi(z))_{(I,s);(J,s')}
\]

(12)

1 This definition of the cluster momenta \( K_n \)'s is not unique, but fixed up to a phase choice \[7\]. Here we limit ourselves to the single set with \( \phi = 0 \), but remark, following Rowlands et al, how a multi-phase reformulation involving averages over possibly other sets can be developed straightforwardly.
we can write down an impurity Green function appropriate to each configuration $\gamma$ of the $N_{\text{sub}} \times N_{c}$ atomic energies at positions $R_{j} + a_{s}$ within a multi-site cluster:

$$G_{i,s}^{(I,s),(J,s')}(z) = \left( G_{\text{av}}^{-1} - \varepsilon_{\gamma}^{-1} \right)_{i,s}^{(I,s),(J,s')} \text{ for } \varepsilon_{\gamma} = \varepsilon_{i,s}^{(I,s)} \delta_{i,j} \delta_{s,s'}$$

(13)

Summing over all of these with an appropriate probability distribution $P(\gamma)$ gives an improved expression for the bulk-averaged propagator:

$$\overline{G}_{(I,s),(J,s')}(z) = \sum_{\gamma} N_{\text{tot}} P(\gamma) G_{(I,s),(J,s')}(\gamma)(z) \text{ with } N_{\text{tot}} = \prod_{s=1}^{N_{\text{sub}}^N_{c}}$$

(14)

enforcing at this stage the possible inclusion of SRO and/or sublattice-specific effects, as illustrated in the examples of section 4.

This result provides a new starting point for the iterative determination of a better effective medium description. The algorithm is applied at each energy beginning from an arbitrary Ansatz for the self-energy in eq. 10 and computing a new $\Xi$ as:

$$\Xi_{(I,s),(J,s')}(z) = \left( G_{\text{av}}^{-1}(z) - \overline{G}(z) \right)_{(I,s),(J,s')}$$

(15)

to re-evaluate the lattice Fourier transform of eq. 8 and following steps until an arbitrary degree of self-consistency is achieved.

4. Numerical results and discussion

4.1. Validation studies

As a check, the method can be examined for its ability to reproduce the CPA results in the special case $N_{\text{sub}} = 1$, $N_{c} = 1$. This is illustrated by comparing the DOS obtained from an independent implementation of the original algorithm [22], with a study of the same single sublattice system for varying cavity sizes in the new method (figure 2).

We consider then the case of a possibly complex material with $N_{\text{sub}} \geq 1$ sites per unit cell. Under the special constraint of every sublattice hosting only the same alternative on-site energies $\epsilon_{i,s} = \epsilon_{i,s'}$ for $s = 1, \ldots, N_{\text{sub}}$ (degenerate scenario), the effective medium has the same translational invariance as the lattice spanned by vectors $R_{(i,s)} = R_{i} + a_{s}$, and the self-energy can be written as:

$$\Xi_{s,s'}(K_{n},z) = \frac{1}{N_{\text{sub}}} \sum_{g_{l}}^{N_{\text{sub}}} \Xi(K_{n} + g_{l},z)e^{-ig_{l}(a_{s} - a_{s'})}$$

(16)

for $g_{l}$ reciprocal space (sub)lattice vectors. Combining this with eq. 8 gives:

$$\Xi_{(I,s),(J,s')}(z) = \frac{1}{N_{c}N_{\text{sub}}} \sum_{K_{n}}^{N_{c}} \sum_{g_{l}}^{N_{\text{sub}}} \Xi(K_{n} + g_{l},z)e^{+i(K_{n} + g_{l})(R_{I} + a_{s} - R_{J} - a_{s'})}$$

(17)

and similar expressions are appropriate for $G_{(I,s),(J,s')}(z)$ or $G_{s,s'}(K_{n},z)$, showing how in this limit a MS-NL-CPA $N_{\text{sub}}$ sites per unit cell $N_{c} = 1$ single tile calculation can be equivalently decomposed into a NL-CPA study with $N_{c}$ tiles over a simple $N_{\text{sub}} = 1$ lattice, or intermediate cases (table 1). This is illustrated in figure 3 comparing three possibilities for a cavity of 4 elements.
The density of states vs. energy (evaluated at $z = \epsilon + i\eta$ for $\eta = 0.05t$) for the model of eq. 1 in the simple unit cell case $N_{\text{sub}} = 1$, with on-site energies $\epsilon_A = -2t$, $\epsilon_B = +2t$ for a 1D compound $A_cB_{1-c}$. Calculations at varying concentrations $c = 0.0, 0.25, 0.5, 0.75, 1.0$ with the original CPA and NL-CPA algorithms, in an equivalent SRO = 0 regime (see text) and for different cavity sizes. The CPA results are perfectly reproduced for $N_c = 1$ (black). Going beyond the single-site treatment to $N_c = 2$ (red) and above allows to pick up additional features in the presence of disorder.

| NL-CPA          | MS-NL-CPA          |
|-----------------|--------------------|
| $N_c = 2, N_{\text{sub}} = 1$ | $N_c = 1, N_{\text{sub}} = 2$ |
| $N_c = 4, N_{\text{sub}} = 1$ | $N_c = 2, N_{\text{sub}} = 2$ |
|                 | $N_c = 1, N_{\text{sub}} = 4$ |
| $N_c = 8, N_{\text{sub}} = 1$ | $N_c = 4, N_{\text{sub}} = 2$ |
|                 | $N_c = 2, N_{\text{sub}} = 4$ |
|                 | $N_c = 1, N_{\text{sub}} = 8$ |

Table 1. Equivalent MS-NL-CPA descriptions in the particular case of a degenerate scenario, explicitly listed up to a total computational budget of $N_{\text{sub}} \times N_c = 8$ sites.

4.2. Complex unit cell, multi-site treatment

Following the previous validation tests in the degenerate limit, we now investigate sublattice dependent disorder effects, with specific on-site energies on the different sublattices. The extended MS-NL-CPA treatment enables an accurate study of the effect of selective disorder, together with SRO; specific examples are discussed in section 4.2.1.

As a bi-product of the development we point out that it is also possible to trade unit cell complexity (larger $N_{\text{sub}}$) for a simplification in the Brillouin zone tiling procedure (lower $N_c$). A sample application of this approach in the context of disorder-to-order phase transitions is illustrated in section 4.2.2.

4.2.1. Sublattice-selective doping with SRO

For a first fully representative test system for the MS-NL-CPA we consider a complex unit cell material, with different on-site energies $\epsilon_A, \epsilon_B$ and $\epsilon_C, \epsilon_D$ for atoms belonging to two sublattices.
Figure 3. NL-CPA ($N_c = 4$, $N_{sub} = 1$, black), MS-NL-CPA ($N_c = 2$, $N_{sub} = 2$, green) and MS-NL-CPA ($N_c = 1$, $N_{sub} = 4$, blue) DOS for the same model setup as figure 2 evaluated for a degenerate test case $\epsilon_{(i,s)} = \epsilon_{(i,s')} \forall s = 1, \ldots, N_{sub}$. In the simple unit cell treatment with $N_{sub} = 1$ the larger cavity size allows to resolve additional short length scale features. The same results are obtained from the equivalent decomposition in $N_{sub} = 2$ or $N_{sub} = 4$ sublattices, lying on top of each other for this degenerate scenario, as the total cavity size is kept constant.

Figures 4-6 illustrate the impact of various SRO regimes, evaluated for a multi-site cavity size of $N_c = 2$ elements, and in the particular example of a selectively doped compound. Sublattice $s = 1$ hosts a regular array of species $A$, with on-site energies $\epsilon_A = -2t$. A disordered distribution of impurities ($C_{2}, D_{1-c_{2}}$), with $\epsilon_C = +1t$, $\epsilon_D = +3t$, occurs instead with varying concentration $c_2 = 0, 0.25, 5, 75, 1$ on sublattice $s = 2$ alone.

The non-local nature of the method allows to investigate the effect of different biases in the average dispersion of the dopant. We consider in particular two extremal cases from the whole series of physical possibilities.

In a total clustering regime ($SRO = +1$) or multi-site probability distribution $P(\gamma) = c_2$ if $\epsilon_{(I,2)} = \epsilon_C$, or $P(\gamma) = 1 - c_2$ if $\epsilon_{(I,2)} = \epsilon_D \forall I = 1, \ldots, N_c$, and $P(\gamma) = 0$ otherwise, figure 4 similar atomic species show a tendency towards phase segregation into local regions of homogeneous elements. This creates the conditions for a DOS dominated by superposition of the typical 1D Van Hove singularities for individually pure systems, centered on each constituent on-site energy at $\epsilon = -2t$ (ordered sublattice, in red) and $\epsilon = +1t$ or $\epsilon = +3t$ (disordered sublattice, in green), with a relative contribution proportional to the concentration $c_2$ or $1 - c_2$. The initial gap is progressively narrowed down from $\Delta \epsilon \simeq 5t$ for a pure $(A), (D)$ system, to $\Delta \epsilon \simeq 3t$ for the pure $(A), (C)$ one. This takes place through the growth of intermediate states that carry the features associated with unperturbed 1D hopping between like neighbors on sublattice 2 (all $C$ or all $D$, in the homogeneous background of interleaved $A$ elements on the other sublattice).

The opposite case of a total ordering regime ($SRO = -1$) or $P(\gamma) = c_2$ if $\epsilon_{(I,2)} = \epsilon_C; \epsilon_{(I+1,2)} = \epsilon_D; \epsilon_{(I+2,2)} = \epsilon_C, \ldots$, and $P(\gamma) = 1 - c_2$ if $\epsilon_{(I,2)} = \epsilon_D; \epsilon_{(I+1,2)} = \epsilon_C; \epsilon_{(I+2,2)} = \epsilon_D, \ldots$, and $P(\gamma) = 0$ otherwise, figure 5 provides a qualitatively different outlook. Here contiguity between unlike elements is favored. Since the surrounding sites around the minority impurity ($C$ for concentration $c_2 < 50\%$, $D$ for $c_2 > 50\%$) are always occupied by different neighbors, hopping processes respectively associated with its on-site energy $\epsilon_C$ or $\epsilon_D$ are strongly
Figure 4. Selective doping with clustering of impurities ($SRO = +1$): DOS for a $N_{sub} = 2$, $N_c = 2$ study of a complex unit cell compound with distinct on-site energies and disorder (sublattice $s = 1$: $\epsilon_{i,s=1} = \epsilon_A = -2t \forall i$, red; sublattice $s = 2$: $\epsilon_{i,s=2} = \epsilon_C = +1t$ or $\epsilon_D = +3t$ with concentration $c_2 = 0.0, 0.25, 0.5, 0.75, 1.0$, green), favoring contiguous alike elements.

suppressed, leading to a DOS contribution in the form of an impurity -like single peak around its energy $\epsilon = +1t$ or $\epsilon = +3t$. The same argument however is reversed for the majority species $D$ or $C$, giving rise to an almost pure, Van Hove -like double feature around that energy. The transition takes place through the special concentration value $c_2 = 50\%$, for which both species of sublattice $s = 2$ are equally localized, and correspondingly two single peaks appear.

We also note that in both cases of the series in figure 4 and 5 some SRO -induced differences also extend to the DOS contributions from the ordered sublattice $s = 1$ (red). In the presence of impurity clustering on sublattice $s = 2$, atoms belonging to the orderly distributed species $A$ find themselves on average surrounded by extended domains of homogeneously different background $\epsilon_{i,(s=2)} = \epsilon_C$ or $\epsilon_{i,(s=2)} = \epsilon_D$. This can be expected to impact hopping processes at the effective medium level, giving raise to the peculiar superposition of localized/delocalized features around the original on-site energy $\epsilon = -2t$ (figure 4). The effect is different in nature, and on the whole less appreciable, in a $SRO = -1$ regime, where as remarked an atom of species $A$ tends to always appear within a similar environment of species $C$ on one side, $D$ on the other one, and vice-versa. This affects only subtly delocalization, which remains the dominant process on the sublattice, and results in a contribution mainly sensitive to the 1D nature of the model. Such developments may prove useful in some materials cases, in order to gain a measure of control over the contribution from the otherwise ordered and more stable constituents of a complex compound, by means of annealing or cold-working procedures having a larger impact on the disordered sublattice.

These calculations can be contrasted with a totally uncorrelated setup ($SRO = 0$) or $P(\gamma) = \prod_{i=1}^{N_c} (c_2)$ if $\epsilon_{(i,2)} = \epsilon_C$, $(1 - c_2)$ if $\epsilon_{(i,2)} = \epsilon_D$, mimicking the single-site design of the MS-CPA. In the absence of any particular short range ordering on the doped sublattice $s = 2$, the higher resolution physical features resolved in both figure 4 and 5 appear to be contained in nuce and superimposed within the DOS of figure 6. As discussed above, their relative importance follows the bias towards total clustering or total ordering. These differences are enhanced by the unidimensional nature of the TB model adopted in this exposition, but further studies from
Figure 5. Selective doping with local ordering of impurities ($SRO = -1$): DOS for a $N_{sub} = 2$, $N_c = 2$ study of a complex unit cell compound with distinct on-site energies and disorder (sublattice $s = 1$: $\epsilon_{(i,s=1)} = \epsilon_A = -2t \ \forall i$, red; sublattice $s = 2$: $\epsilon_{(i,s=2)} = \epsilon_C = +1t$ or $\epsilon_D = +3t$ with concentration $c_2 = 0.0, 0.25, 0.5, 0.75, 1.0$, green), favoring contiguous dissimilar elements.

a fully 3D reimplementation of the theory in a multiple scattering formalism for first-principles investigations also confirm their persistence in the case of realistic materials.

Figure 6. Selective doping with totally uncorrelated impurities ($SRO = 0$): DOS for a $N_{sub} = 2$, $N_c = 2$ study of a complex unit cell compound with distinct on-site energies and disorder (sublattice $s = 1$: $\epsilon_{(i,s=1)} = \epsilon_A = -2t \ \forall i$, red; sublattice $s = 2$: $\epsilon_{(i,s=2)} = \epsilon_C = +1t$ or $\epsilon_D = +3t$ with concentration $c_2 = 0.0, 0.25, 0.5, 0.75, 1.0$, green)
4.2.2. Order-disorder transition scenario

If a homogeneously disordered system is cooled through a phase transition, the underlying symmetry is broken and long range order (LRO) develops and grows as the temperature is lowered towards 0K. In our second example we use the model of eq. 1 to examine such scenario, considering again similar on-site energies on both sublattices $\epsilon_A = \epsilon_C = -2t$, $\epsilon_B = \epsilon_D = +2t$ as in the degenerate test cases of figure 3, but adopting here constituents probability distributions $P(\gamma)$ governed by the coupled concentrations: $c_2 = 1 - c_1 = (1 - \eta)/2$.

In this setup $\eta$ is a LRO parameter, ranging from 0 to 1 as a fixed 1 : 1 ratio ($A, D$) binary alloy stabilizes into more and more regular structures, up to the totally ordered limit. Figure 7 illustrates the effect of such modifications on the DOS, starting from the same totally uncorrelated results also obtained in the central panel of figure 3 for a $c = 0.5$, simple unit cell $N_c = 4$ NL-CPA calculation. Using now an additional resolution into two sublattices as afforded by the MS-NL-CPA, it is possible to investigate this disorder-to-order transition through the $N_c = 2, N_{sub} = 2$ decomposition suggested in table 1.

As the order parameter increases, we can follow the evolution of the most significant DOS features associated with on-site energies $\epsilon_A, \epsilon_D$. In the leftmost panel interactions with totally uncorrelated random neighbours are responsible for a pronounced smearing and broadening of the states around $\epsilon = \pm 2t$. Both sublattices present an exactly equivalent environment, and give therefore contributions lying again on top of each others.

A more and more regular distribution of the same ratio of species $A$ and $D$ into well defined atomic sites at $a_s$ and $a_{s'}$ shows how this picture develops towards the pure scenario (rightmost panel). Disorder tends to gradually fill the initially empty gap between distinct Van Hove singularities, through the insurgence of impurity -like states similarly to the situation observed for the cases of figures 4-6. Here however the peculiarity of coupled concentrations and same on-site energies for both sublattices gives raise to such structures in the form of resonant peaks, occurring approximately at $\epsilon = \pm 4t$ and 0. Considering in particular the intermediate regimes, we note how these differ qualitatively from the on-site states, which remain down to $\eta = 0$.

![Figure 7](image-url)
dominated by different individual sublattices contributions (either red or green). The additional features are instead characterized by finding their origin equally on both sites (green and red lines lying almost on top of each others, panels 2-4), and growing at the expense of the local "matching" species (green for sublattice \( s = 1 \) at \( \epsilon = -2t \), red for \( s = 2 \) at \( \epsilon = +2t \)), while the importance of the alternate one (red for sublattice \( s = 1 \) at \( \epsilon = -2t \), and vice-versa) remains relatively unchanged.

This can be qualitatively explained by comparing the ordered \( \eta = 1 \) sequence: \( \ldots \), \([\epsilon_A, \epsilon_D], [\epsilon_A, \epsilon_D], [\epsilon_A, \epsilon_D], \ldots \) with a possible realization of the central panel case \( c_1 = 0.25 \) or \( \eta = 0.5 \): \( \ldots , [\epsilon_A, \epsilon_D], [\epsilon_D, \epsilon_A], [\epsilon_D, \epsilon_A], [\epsilon_D, \epsilon_A], \ldots \), adopting here the \([\cdot]\) notation to outline the choice of a \( N_{sub} = 2 \) reference unit cell.

The instances of unperturbed intra-sublattice propagation between equivalent species \( A \) at \( a_s \) or \( D \) at \( a_{s'}, \) which are the main factors responsible for the Van Hove double peaks probing the model dimensionality around \( \epsilon = \pm 2t \), get reduced on each sublattice proportionally to the anti-site defects concentration \( c_1 \) or \( c_2 \), until acquiring an almost localized -only aspect (leftmost panel). In the same energy subregion the contribution from the other site is instead always impurity -like, reflecting the interleaved nature of this particular model setup. As opposed to the example of figure \( 3 \) here in fact free propagation is always hindered by a different species even in the “pure” limit. This results in the superposition of a similar dominant symmetric structure for each sublattice, on top of an asymmetric one from the other, giving the skewed aspect also seen in the previous series (figures 4-6, leftmost and rightmost panels).

On the other hand, the progressive collapse of LRO in a system of equidistant sites at \( 0, L = 2a, 2L = 4a, \ldots \), with the same possible on-site energies for both sublattices, can only take place by opening up more and more nearest neighbour propagation channels at the new halved wavelength \( a_c \). Replacing any atom \( A \) with its alternative \( D \) will always result in having two equivalent elements next to each other across the arbitrary unit cell twice, somewhere in the bulk; and the translational invariant effective medium treatment is insensitive to the actual different placement of such \( \ldots , A[, A, \ldots and \ldots , D][D, \ldots \) regions, which therefore appear in the DOS equally from both sublattices. Going beyond to \( N_c = 4 \) and above in the non-local expansion of the investigation also confirms the propagation -like nature of these extra peaks, already hinted in figure \( 7 \). As the calculation becomes even more resolved, these in fact split again following the expected Van Hove behaviour, while the main on-site features at \( \epsilon = \pm 2t \) retain their single sublattice origin.

5. Conclusions
The recently proposed NL-CPA method for describing disordered electron systems with short-range order can be straightforwardly extended to describe materials with multi-atom per unit cell lattice structures. In many crystalline systems the distribution of impurities on a subset of the sublattices can modify properties nominally associated with the chemical composition of the others. In this paper we have shown how to approach a quantitative analysis of such effects.

The method has been introduced through the language of Green function theory, discussing in particular numerical results from an illustrative 1D implementation. Topical examples from the context of selectively doped materials and the case of disorder-to-order phase transitions show how subtle modifications to an originally single-site effective medium description become accessible, and can be resolved into their specific origin at the level of average local alterations to the microscopic environment in the sample.

Work is in progress on the application of the theory to a multiple scattering (KKR), fully ab-initio treatment of realistic materials.
Acknowledgments
The authors wish to thank Dr. Martin Lüders and Dr. Arthur Ernst for insightful discussions throughout the ongoing development of this work.

Technical support from the Centre for Scientific Computing at the University of Warwick is gratefully acknowledged.

References
[1] Soven P 1967 Phys. Rev. 156 809–813
[2] Gyorffy B and Stocks G 1978 First principles band theory for random metallic alloys Electrons in disordered metals and at metallic surfaces NATO advanced study institutes series ed Phariseau P, Gyorffy B and Scheire L NATO Scientific Affairs Division (Plenum Press)
[3] Faulkner J S and Stocks G M 1980 Phys. Rev. B 21 3222–3244
[4] Rowlands D A, Staunton J B and Gyorffy B L 2003 Phys. Rev. B 67 ISSN 1098-0121
[5] Rowlands D A, Staunton J B, Gyorffy B L, Bruno E and Ginatempo B 2005 Phys. Rev. B 72 045101 ISSN 1098-0121
[6] Rowlands D A 2006 Psi-k newsletter 77
[7] Rowlands D A, Zhang X G and Gonis A 2008 Phys. Rev. B 78 115119
[8] Tulip P R, Staunton J B, Rowlands D A, Gyorffy B L, Bruno E and Ginatempo B 2006 Phys. Rev. B 73 205109
[9] Tulip P R, Staunton J B, Lowitzer S, Ködderitzsch D and Ebert H 2008 Phys. Rev. B 77 165116
[10] Leslie M and Gillan N J 1985 J. Phys. C: Solid State Physics 18 973
[11] Makov G and Payne M C 1995 Phys. Rev. B 51 4014–4022
[12] Freysoldt C, Neugebauer J and Van de Walle C G 2009 Phys. Rev. Lett. 102 016402
[13] Jarrell M and Krishnamurthy H 2001 Phys. Rev. B 63 125102
[14] Rowlands D A, Ernst A, Gyorffy B L and Staunton J B 2006 Phys. Rev. B 73 165122
[15] Lowitzer S, Ködderitzsch D, Ebert H, Tulip P R, Marmodoro A and Staunton J 2010 EPL 92
[16] Pindor A J, Temmerman W M and Gyorffy B L 1983 J. Phys. F: Met. Phys. 13 1627–1644
[17] Temmerman W M and Pindor A J J. Phys. F: Met. Phys. 13 1869
[18] Däne M, Lüders M, Ernst A, Ködderitzsch D, Temmerman W M, Szotek Z and Hergert W 2009 J. Phys.: Cond. Mat. 21 045604
[19] Gyorffy B L, Pindor A, Staunton J B, Stocks G and Winter H 1985 J. Phys.: Cond. Mat. 15 1337
[20] Kudrnovský J, Drelal V and Bruno P 2008 Phys. Rev. B 77 224422
[21] Bellaiche L, Garcia A and Vanderbilt D 2000 Phys. Rev. Lett. 84 5247
[22] Gonis A 1992 Green functions for ordered and disordered systems (North-Holland)