Augmented-space recursion for partially disordered systems

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Atisdipankar Chakrabarti and Abhijit Mookerjee

S N Bose National Centre for Basic Sciences, Block-JD, Sector-III, Kolkata-700098, India

E-mail: adc@boson.bose.res.in (A Chakrabarti) and abhijit@boson.bose.res.in (A Mookerjee)

Abstract
Off-stoichiometric alloys exhibit partial disorder, in the sense that only some of the sublattices of the stoichiometric ordered alloy become disordered. This paper puts forward a generalization of the augmented-space recursion introduced earlier by Saha and Mookerjee (Saha T and Mookerjee A 1997 *J. Phys.: Condens. Matter* **10** 2179) for systems with many atoms per unit cell.

1. Introduction

Binary alloys in stoichiometric compositions invariably exhibit ordered structures at low temperatures. As we depart from perfect stoichiometric compositions, it is not possible to populate the lattice in the given compositions so as to produce a perfectly ordered structure. Take, for example, a $B_{75}A_{25}$ binary alloy on a fcc lattice. One of the possible stable ordered phases is the L12 arrangement as shown in figure 1. An example of this is provided by Cu_3Au. In a cubic unit cell the corner is occupied by an A atom, while the three face centres are occupied by B atoms. Since there are N corners and $3N$ face centres (N being the total number of unit cells in the solid) and exactly as many A and B atoms, at this composition the L12 ordered arrangement exactly populates all the lattice sites. Ordered arrangement becomes impossible for, say, $B_{70}A_{30}$. However, the following arrangement becomes possible: since there are now
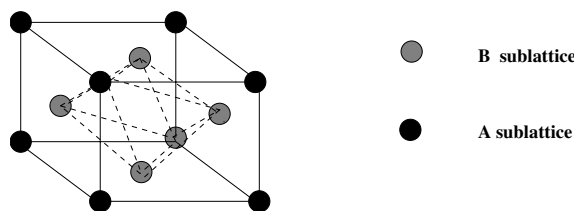

Figure 1. The L12 atomic arrangement for 75–25 AB binary alloys on a fcc lattice.

$1.2N$ A atoms, N of them may occupy the N corners. The $3N$ face centres may be occupied randomly by the $2.8N$ B atoms and $0.2N$ remaining A atoms. The original A sublattice remains ordered, while the B sublattice becomes disordered. Since there are on the whole $3N$ face centres, the occupation probabilities of the A and B atoms in this sublattice are $0.9\dot{3}$ and $0.0\dot{6}$ respectively. This arrangement is quite different from that of the completely random alloy, where all sites are randomly occupied by either the A or B atoms with probabilities 0.3 and 0.7 respectively. It is also rather different from the *partial disorder* defined by [9]. In this communication we shall define *partial disorder* in the manner described above.

The recursion method was introduced by [6, 7] as a convenient and numerically efficient method for calculating Green functions and real physical properties like the local density of states (LDOS), the Fermi energy and the band energy. The method comes into its own in situations where translation symmetry of the potential in an effective one-electron Hamiltonian is lost. The Bloch theorem is violated, and we cannot employ the standard reciprocal-space techniques unless we apply a homogeneity-restoring mean-field approximation (like the coherent potential approximation, CPA). This can happen, for instance, at a surface or in a random alloy. In particular, if the ion cores sit on a topologically distorted network or at a rough surface or interface, the recursion method seems the only natural way of dealing with electronic property calculations.

There exists a large body of literature on the application of the recursion method to various situations [8]. For substitutional disorder, the recursion method has been employed in tandem with the augmented-space formalism [10–14] (augmented-space recursion or ASR) for dealing with random alloys, taking into account local configuration fluctuations like chemical clustering, local lattice distortions due to size effects and inhomogeneous randomness at a surface caused by surface segregation. In spite of this extensive body of literature, the recursion method does not seem to have gained wide acceptability in the electronic structure community, and one often has had to face scepticism regarding its accuracy and feasibility when applying it with sophisticated electronic structure techniques to realistic systems.

In this communication we shall first present the ASR in detail for the most general case of systems with many atoms per unit cell. Our subsequent aim will be to study partially disordered systems in alloys with off-stoichiometric compositions. Then we shall apply it to a toy model for partial disorder before carrying on to address realistic systems.

2. Generalized augmented-space recursion within the TB-LMTO formalism

In earlier works [12–14] it has been established that for a disordered system the augmented-space theorem maps a disordered Hamiltonian described in a Hilbert space H onto an ordered Hamiltonian in an enlarged space Ψ, where the space Ψ is constructed by augmenting the configuration space Φ of the random variables of the disordered Hamiltonian together with the Hilbert space H of the disordered Hamiltonian. Thus $\Psi = \Phi \otimes H$. The configuration averaging of the Green function reduces to the evaluation of a particular matrix element of the resolvent of this enlarged Hamiltonian in the augmented space. Hence, if one performs a recursion in the augmented space, one can obtain the matrix element necessary to calculate the configuration average of a Green function directly. The advantage of this method is that it does not involve a single-site approximation or the solution of any self-consistent equation (which is a prerequisite for the CPA and its generalizations). Furthermore, one can treat both diagonal and off-diagonal disorder on an equal footing.

As mentioned earlier, since the recursion method needs a localized, short-ranged basis for its operation, one can implement augmented-space recursion in the framework of the

TB-LMTO formalism. We now describe the methodology of generalized augmented-space recursion in the framework of the TB-LMTO formalism.

The second-order TB-LMTO Hamiltonian is written in terms of potential parameters and the screened structure matrix. For a random binary alloy $A_x B_y$, the LMTO Hamiltonian in the most localized representation is given by

$$\mathcal{H}^{(2)} = E_\nu + h - hoh \tag{1}$$

where

$$h = \sum_{RL\alpha}(\tilde{\mathbf{C}}_{RL\alpha} - \tilde{\mathbf{E}}_{RL\alpha})\mathcal{P}_{RL\alpha} + \sum_{RL\alpha}\sum_{R'L'\alpha'} \tilde{\boldsymbol{\Delta}}_{RL\alpha}^{1/2} S_{RL\alpha,R'L'\alpha'} \tilde{\boldsymbol{\Delta}}_{R'L'\alpha'}^{1/2} \mathcal{T}_{RL\alpha,R'L'\alpha'}. \tag{2}$$

$\mathbf{C}$, $\mathbf{o}$ and $\boldsymbol{\Delta}$ are potential parameters of the TB-LMTO method; these are diagonal matrices in the angular momentum indices. Also $\mathbf{o}^{-1}$ has the dimension of energy and is a measure of the energy window around $\tilde{E}$ within which the approximate Hamiltonian $\mathcal{H}^{(2)}$ is reliable. Also,

$$\tilde{\mathbf{C}}_{RL\alpha} = C_L^A n_R^\alpha + C_L^B(1 - n_R^\alpha) = C_L^B + \delta C_L\, n_R^\alpha$$

$$\delta C_L = C_L^A - C_L^B$$

$$\tilde{\boldsymbol{\Delta}}_{RL\alpha}^{1/2} = (\Delta_L^A)^{1/2} n_R^\alpha + (\Delta_L^B)^{1/2}(1 - n_R^\alpha) = (\Delta_L^B)^{1/2} + \delta\Delta_L^{1/2}\, n_R^\alpha$$

$$\delta\Delta_L^{1/2} = (\Delta_L^A)^{1/2} - (\Delta_L^B)^{1/2}$$

$$\tilde{\mathbf{o}}_{RL\alpha} = o_L^A n_R^\alpha + o_L^B(1 - n_R^\alpha) = o_L^B + \delta o_L\, n_R^\alpha$$

$$\delta o_L = o_L^A - o_L^B$$

$$\tilde{\mathbf{E}}_{\nu RL\alpha} = E_{\nu L\alpha}^A n_R^\alpha + E_{\nu L\alpha}^B(1 - n_R^\alpha) = E_{\nu L\alpha}^B - \delta E_{\nu L\alpha}\, n_R^\alpha$$

$$\delta E_{\nu L\alpha} = E_{\nu L\alpha}^A - E_{\nu L\alpha}^B.$$

R denotes a *cell position* label associated with a TB-LMTO basis and $L = (\ell m m_s)$ is the composite angular momentum index. α denotes an atom in the Rth cell whose position is $R + \xi^\alpha$. n_R^α is the site-occupation variable which takes values 0 or 1 depending upon whether site α in the Rth cell is occupied by an A or a B atom. For *partial disorder*, this is a random variable whose probability density depends upon which sublattice it belongs to; hence the label α associated with it. The structure matrix $S_{RL\alpha,R'L'\alpha'}$ is non-random in the case of substitutional alloys with negligible size mismatch. Now one can obtain the full $\mathcal{H}^2$ by inserting h in expression (1).

$\mathcal{P}_{RL\alpha}$ and $\mathcal{T}_{RL\alpha,R'L'\alpha'}$ are the projection and transfer operators in Hilbert space H spanned by the tight-binding basis $\{|RL\alpha\rangle\}$.

The expanded Hamiltonian $\hat{\mathcal{H}}$ in the augmented space is constructed by replacing the random site-occupation variable n_R^α by its corresponding operator representation $\mathcal{M}_R^\alpha$ in configuration space, where $\mathcal{M}_R^\alpha$ is given by

$$\mathcal{M}_R^\alpha = x_A^\alpha \mathcal{P}_{R\alpha}^\uparrow + x_B^\alpha \mathcal{P}_{R\alpha}^\downarrow + \sqrt{(x_A^\alpha x_B^\alpha)}(\mathcal{T}_{R\alpha}^{\uparrow\downarrow} + \mathcal{T}_{R\alpha}^{\downarrow\uparrow}).$$

In the presence of off-diagonal disorder, which is invariably present in the form of the TB-LMTO Hamiltonian, even reduction of the rank of the invariant subspace on which recursion acts, using the symmetries of the augmented space, does not allow us to sample as many configuration states as we would like. This is because, as recursion proceeds, the number of configuration states sampled at the nth step of recursion becomes unmanageably large when $n > 5$ (for example). To do away with this problem, the working equations are transformed so as to put the Hamiltonian for the recursion in an effective diagonal disorder form. This allows one to sample further shells in augmented space and to confirm the shell convergence of the recursion.

To do this, we first suppress all the indices and write the expression for the resolvent as follows:

$$(E - \mathcal{H}^{(2)})^{-1} = (E - \tilde{\mathbf{C}} - \tilde{\boldsymbol{\Delta}}^{1/2} S \tilde{\boldsymbol{\Delta}}^{1/2} + h\tilde{\mathbf{o}}h)^{-1}$$

$$= \tilde{\boldsymbol{\Delta}}^{1/2} \left[\frac{E - \tilde{\mathbf{C}}}{\tilde{\boldsymbol{\Delta}}} - S + \left(\frac{\tilde{\mathbf{C}} - \tilde{\mathbf{E}}_\nu}{\tilde{\boldsymbol{\Delta}}} + S \right)(\tilde{\boldsymbol{\Delta}}^{1/2}\tilde{\mathbf{o}}\tilde{\boldsymbol{\Delta}}^{1/2})\left(\frac{\tilde{\mathbf{C}} - \tilde{\mathbf{E}}_\nu}{\tilde{\boldsymbol{\Delta}}} + S \right) \right]^{-1} \tilde{\boldsymbol{\Delta}}^{1/2}.$$

Using the augmented-space theorem, we can write the expression for the configuration-averaged Green function as

$$\langle\langle G_{RL\alpha, RL\alpha}(E) \rangle\rangle = \langle 1 | \left[\hat{E} - \hat{A} + \hat{B} + \hat{F} - \hat{S} + (\hat{J} + \hat{S})\hat{o}(\hat{J} + \hat{S}) \right]^{-1} | 1 \rangle$$

where

$$|1\rangle = \left\{ \frac{A_L^\alpha(\Delta^{-1/2})}{\left[A_L^\alpha(1/\Delta) \right]^{1/2}} \right\} |R, L, \alpha \otimes \{\emptyset\}\rangle + \left\{ \frac{F_L^\alpha(\Delta^{-1/2})}{\left[A_L^\alpha(1/\Delta) \right]^{1/2}} \right\} |R, L, \alpha \otimes \{R\}\rangle$$

and

$$\hat{A} = \sum_{R,L,\alpha} \left\{ \frac{A_L^\alpha(C/\Delta)}{A_L^\alpha(1/\Delta)} \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L \otimes \mathcal{I}$$

$$\hat{B} = \sum_{R,L,\alpha} \left\{ \frac{B_L^\alpha((E-C)/\Delta)}{A_L^\alpha(1/\Delta)} \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L \otimes \mathcal{P}_{R\alpha}^\downarrow$$

$$\hat{F} = \sum_{R,L,\alpha} \left\{ \frac{F_L^\alpha((E-C)/\Delta)}{A_L^\alpha(1/\Delta)} \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L \otimes (\mathcal{T}_{R\alpha}^{\uparrow\downarrow} + \mathcal{T}_{R\alpha}^{\downarrow\uparrow})$$

$$\hat{S} = \sum_{RL\alpha} \sum_{R'L'\alpha'} \left\{ A_L^\alpha(1/\Delta)^{-1/2} \right\} S_{RL\alpha, R'L'\alpha'} \left\{ A_L^\alpha(1/\Delta)^{-1/2} \right\} \mathcal{T}_{R\alpha, R'\alpha'} \otimes \mathcal{T}_{LL'} \otimes \mathcal{I}.$$

Here, $\hat{J} = \hat{J}_A + \hat{J}_B + \hat{J}_F$ and $\hat{o} = \hat{o}_A + \hat{o}_B + \hat{o}_F$, where

$$\hat{J}_A = \sum_{R,L,\alpha} \left\{ \frac{A_L^\alpha((C - E_\nu)/\Delta)}{A_L^\alpha(1/\Delta)} \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L \otimes \mathcal{I}$$

$$\hat{J}_B = \sum_{R,L,\alpha} \left\{ \frac{B_L^\alpha((C - E_\nu)/\Delta)}{A_L^\alpha(1/\Delta)} \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L \otimes \mathcal{P}_{R\alpha}^\downarrow$$

$$\hat{J}_F = \sum_{R,L,\alpha} \left\{ \frac{F_L^\alpha((C - E_\nu)/\Delta)}{A_L^\alpha(1/\Delta)} \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L \otimes (\mathcal{T}_{R\alpha}^{\uparrow\downarrow} + \mathcal{T}_{R\alpha}^{\downarrow\uparrow})$$

$$\hat{o}_A = \sum_{R,L,\alpha} \left\{ A_L^\alpha(\tilde{o}) A_L^\alpha(1/\Delta) \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L \otimes \mathcal{I}$$

$$\hat{o}_B = \sum_{R,L,\alpha} \left\{ B_L^\alpha(\tilde{o}) A_L^\alpha(1/\Delta) \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L \otimes \mathcal{P}_{R\alpha}^\downarrow$$

$$\hat{o}_F = \sum_{R,L,\alpha} \left\{ F_L^\alpha(\tilde{o}) A_L^\alpha(1/\Delta) \right\} \mathcal{P}_{R,\alpha} \otimes \mathcal{P}_L(\mathcal{T}_{R\alpha}^{\uparrow\downarrow} + \mathcal{T}_{R\alpha}^{\downarrow\uparrow})$$

where

$$A_L^\alpha(Z) = x_A^\alpha Z_L^A + x_B^\alpha Z_L^B$$
$$B_L^\alpha(Z) = (x_B^\alpha - x_A^\alpha)(Z_L^A - Z_L^B)$$
$$F_L^\alpha(Z) = \sqrt{x_A^\alpha x_B^\alpha}(Z_L^A - Z_L^B).$$

Z is any single-site parameter.

Though the computational burden is considerably reduced due to the diagonal formulation, the recursion now becomes energy dependent as is clear from the expressions for $\hat{B}$ and $\hat{F}$ above. The old formalism was free of this constraint. This energy dependence makes the recursion technique rather unsuitable, because now we have to carry out one recursion per energy point of interest. This problem is tackled using the *seed recursion technique* [4]. The idea is to choose a few seed points across the energy spectrum uniformly, carry out recursion on those points and then fit the coefficients of recursion throughout the whole spectrum. In this way one can save hugely on computation time. For example, if one is interested in an energy spectrum of 100 points, in the bare diagonal formulation recursion has to be carried out at all the 100 points but in the seed recursion technique one needs to perform recursions only at 15–20 points. The whole idea stems from the fact that in most of the cases of binary alloys, it is seen that the recursion coefficients α_n and β_n vary quite weakly across the energy spectrum. So, one can easily pick up a few of them and fit throughout the whole range of energy using a suitable function.

3. Calculations on a model system

Before we carry out calculations on a real alloy, let us first apply our formalism to a toy model in order to achieve an understanding of the effects of partial disordering. We shall consider a 50–50 AB alloy ordered first on a square lattice as shown in figure 2 and only s states on this atomic arrangement. The Hamiltonian in a tight-binding basis set is then

$$H = \sum_i \epsilon_{i\alpha,i\alpha'} \mathcal{P}_{i\alpha,i\alpha'} + \sum_{\{ij\}} t_{i\alpha,j\alpha'} \mathcal{T}_{i\alpha,j\alpha'}$$

where $\{ij\}$ denotes that i and j are nearest-neighbour cells on the lattice; α is 1 or 2 according to whether we are referring to the corner atoms or central atoms in a square unit cell (dark and light atoms in figure 2). If we consider only the nearest-neighbour overlaps at a distance $a/\sqrt{2}$ where a is the square-lattice constant, the diagonal and off-diagonal terms of the Hamiltonian are (referring to figure 3)

$$\epsilon_{i\alpha,j\alpha'} = \begin{pmatrix} \epsilon & t \\ t & \epsilon \end{pmatrix}$$

$$t_{i\alpha,j\alpha'} = \begin{pmatrix} 0 & 0 \\ t & 0 \end{pmatrix} \qquad r_i \text{ and } r_j \text{ are in the (10) and (01) directions}$$

$$t_{i\alpha,j\alpha'} = \begin{pmatrix} 0 & t \\ 0 & 0 \end{pmatrix} \qquad r_i \text{ and } r_j \text{ are in the (10) and (01) directions.}$$
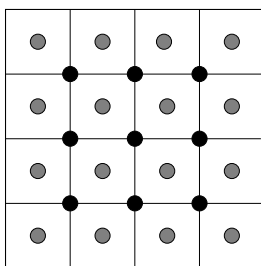
Figure 2. The ordered atomic arrangement on a square lattice for $A_{50}B_{50}$ alloys.

——— t=1 nearest neighbour at ~ 0.7 a

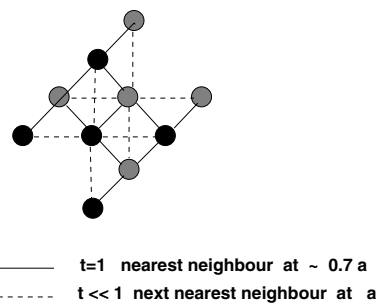- - - - - t << 1 next nearest neighbour at a

Figure 3. Nearest-neighbour overlaps for a central cell in a square lattice with lattice constant of a units.

The ordered lattice has a density of states which has a central band gap with integrable infinite Van Hove singularities at the two internal band edges, two kink singularities within the band and the usual square-root singularities at the external band edges. As expected, the density of states is symmetric about the band centre $\bar{\epsilon} = 0.5$. This is shown in figure 4.
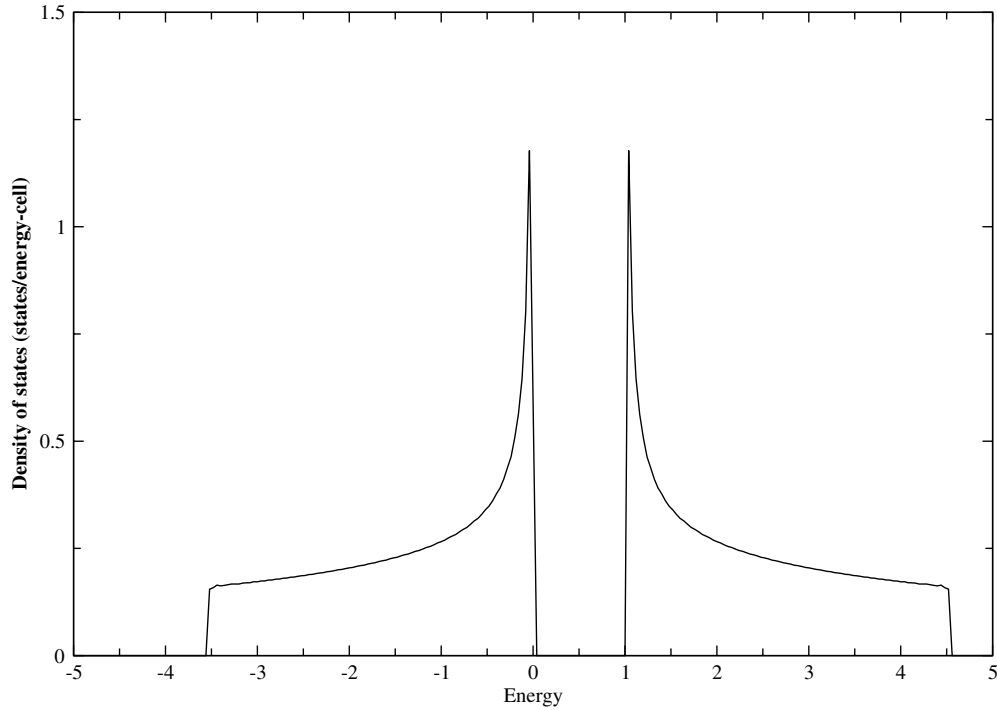

Figure 4. The density of states for the perfectly ordered lattice.

The density of states for the perfectly disordered lattice, where each lattice site is occupied by either an A or a B atom with probabilities proportional to their concentrations, is shown in figure 5. Disorder washes away the Van Hove singularities and the central band gap is filled up. The results are identical to those for a disordered square lattice with lattice vectors $(a/\sqrt{2}, 0)$ and $(0, a/\sqrt{2})$.

The next figure, figure 6, shows the density of states and Fermi energies for the partially disordered half-filled alloys at just off-stoichiometric compositions (49.5–50.5) and (50.5–49.5). Disorder washes out the Van Hove singularities, although vestiges of the kink singularities remain. The signature of the internal infinite singularities shows up as peaks, but disorder fills up the internal band gap. The band-edge square-root singularities remain as artifacts of the termination procedure. Loss of stoichiometry weights the two 'bands' differently, leading to a loss of symmetry about the band centre.

Figure 7 shows the band energy for the partially ordered alloys. There is a jump at the stoichiometric composition with the band energy for the ordered alloy falling halfway between the two branches. This jump can be understood by carefully examining the graphs in the left-hand and right-hand regions of figure 7. The band energy represents the average energy (centre of gravity) of the portion of the graph to the left of the Fermi energy. The density of states in the left-hand region has greater weight below the Fermi energy as compared to that in the right-hand region, ensuring that the band energy is more negative for the compositions shown
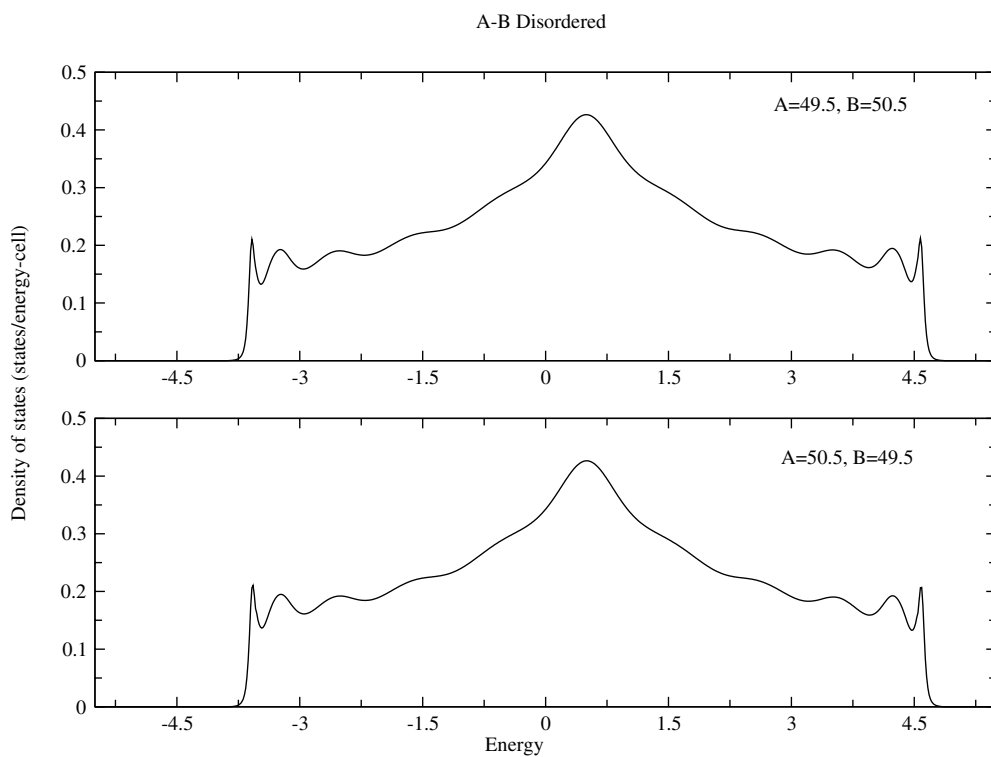
A-B Disordered

Figure 5. Partial densities of states (states/(energy cell)) for the A and B atoms (top, bottom) for a completely disordered alloy at different off-stoichiometric compositions.
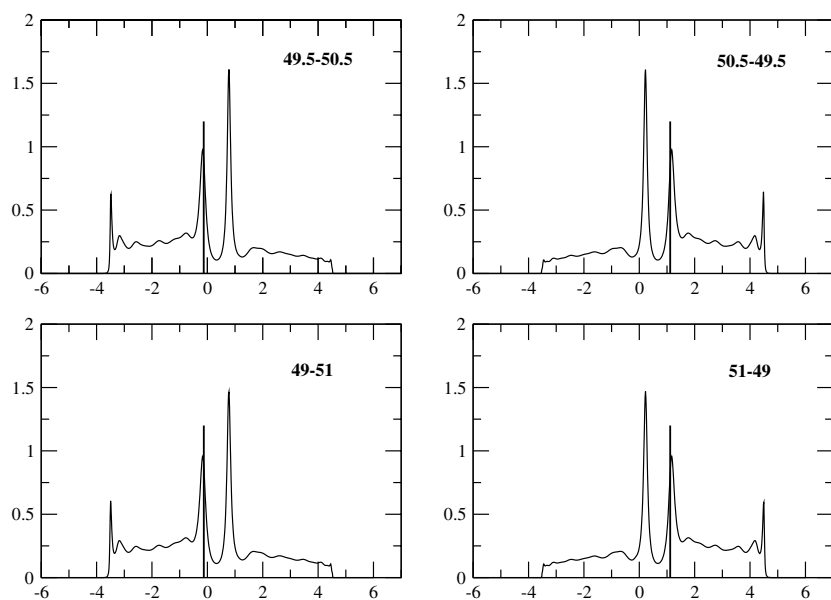

Figure 6. The density of states (states/(energy cell)) for a partially disordered alloy, at different off-stoichiometric compositions.
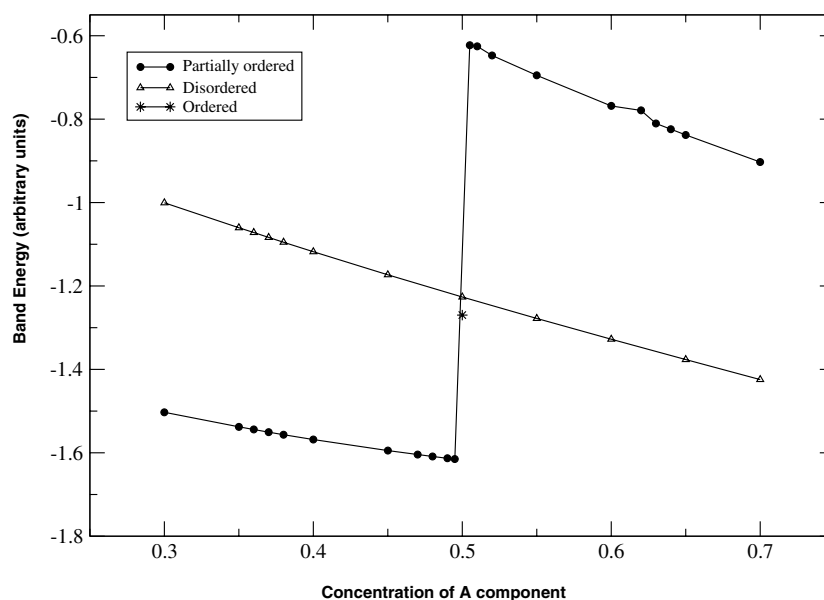
Figure 7. Band energies for the partially ordered, fully ordered and fully disordered alloys at stoichiometric (50–50) and nearby off-stoichiometric compositions.

in the left-hand region. The sudden jump is the result of the Fermi energy shifting across the pseudo-band gap as we cross the 50–50 composition and including the high peak at $E = 0$, which shifts the average energy to higher values. The specific behaviour of the band energy depends sensitively on the features of the density of states. The specific behaviour for our toy model may not obtain for realistic alloy systems.

In contrast, the behaviour of the band energy with composition for the fully disordered alloy is smooth, reflecting the smooth behaviour of the density of states without any internal band gaps. The figure indicates that for compositions to the left of the 50–50 stoichiometric one, the alloy prefers to be partially ordered. At 50–50 the ordered alloy is stable for our toy model, while for compositions to the right of 50–50 the alloy stabilizes in the completely disordered phase.

4. Remarks and conclusions

In this communication we first proposed a generalization of the ASR for partially ordered binary alloy systems. Partial ordering of the type where disorders in different sublattices are different has been studied in particular. Finally, we studied a model system, in order to achieve an understanding of the effects of partial disordering. We are now in a position to apply our formalism to realistic alloy systems. This will be the subject of a future communication.

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