A two-potential embedding approach to the electronic structure of disordered binary alloys

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Abstract. Using an embedding technique introduced in a recent publication by one of us, we study the electronic structure of disordered binary alloys within a pair–cluster coherent potential approximation.

In a recent publication, Mookerjee and Bardhan (1989) have introduced a method for determining the electronic structure of disordered systems that self-consistently takes into account the effect of clusters. The formalism is based on an adaptation to alloy systems of the embedding technique introduced by Inglesfield (1981) for application to problems of interfaces and impurities. The method involves the partition of the Hilbert space in which the Hamiltonian of the Schrödinger equation under study is defined, into two subspaces I and II with an interface S between them. We choose the subspace II in such a way that the wavefunction $\psi(r)$ can be assumed to be known in II and we choose a trial wavefunction $\varphi(r)$ in I that matches with $\psi(r)$ at the interface: $\varphi(r_S) = \psi(r_S)$. We now produce an expression for the matrix element of the Hamiltonian $\mathcal{H}$ and minimise it with respect to variations of the trial wavefunction $\varphi(r)$. The mathematics of the process has been described in detail in the papers of Inglesfield (1981) and Mookerjee and Bardhan (1989). We end up with an effective Schrödinger equation with its effective $\mathcal{H}' \in I$:

$$\left(-\tfrac{1}{2}\nabla^2 + V(r) - E\right)\varphi(r) + \tfrac{1}{2}\delta(n - n_S)\,\partial\varphi/\partial n_S + \delta(n - n_S)\int d^2r_S K(r_S, r_S')\varphi(r_S') = 0$$

or

$$(\mathcal{H}' - E)\varphi(r) = 0. \tag{1}$$

The second term ensures that $\mathcal{H}'$ is Hermitian in the subspace I alone, and the third term is a surface potential which describes the effect of I being embedded in the space II. The eigenfunctions and eigenvalues of the above Schrödinger equation, defined only on the subspace I, are the solutions of the original full Schrödinger equation. The function $K(r, r')$ is the functional inverse of the Green function $G(r, r')$ satisfying

$$\left(-\tfrac{1}{2}\nabla^2 + V(r) - E\right) G(r, r') = \delta(r - r')$$

with $r, r' \in II$ *alone*.

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The Green function $G(r, r')$ satisfies the usual boundary condition at infinity, but also satisfies the Neumann boundary condition that its normal derivative $\partial G/\partial n_S = 0$ on the interface S.

For a disordered alloy the region I is chosen to be a cluster of, say, *muffin-tin* potentials. Usually the shape of the interface S of a cluster is quite complicated and the construction of the relevant Green function $G(r, r')$ with Neumann boundary conditions on it is difficult. In practice, one could take S to be a spherical surface that just contains the cluster under study. If we now introduce in I an overcomplete basis set to represent our Schrödinger equation, so that the optimal boundary condition on S may be satisfied, we do not usually face problems—we know this from the extensive applications to surfaces described by Inglesfield. In that case, it is also true that the interface S is never a plane, and is quite often *corrugated*. The bounding plane is chosen to be S and an overcomplete basis set is chosen in the semi-infinite I.

In II we replace the disordered potential $V(r)$ by a cluster translationally symmetric coherent potential $V_{coh}(r, E)$. The coherent potential is obtained from the fact that if we now embed in this *effective medium* II a cluster with a particular configuration σ, then the extra scattering that the electron will suffer because of this added *impurity* is *on average* zero.

$$\langle \mathbb{G}(r, r', V_\sigma, V_{coh}) \rangle_\sigma = \mathbb{G}_0(r, r', V_{coh}) \tag{2}$$

where $(\mathcal{H}' - E\mathbb{I})\mathbb{G}(r, r') = \delta(r - r')$, while $\mathbb{G}_0(r, r')$ is obtained from a Hamiltonian where the coherent potential $V_{coh}(r, E)$ is substituted for the entire potential $V(r)$. From (1) we see that $\mathcal{H}'$ and hence also $\mathbb{G}$ depend on both V_σ of the cluster in I and V_{coh} through their dependence on K. $\langle\ \rangle_\sigma$ denotes the average over the configurations σ. For a binary alloy σ can take 2^n values for a cluster of size n, and the relevant probability is $x_A^m x_B^{m'}$, where there are m A-type atoms and m' B-type atoms in the cluster and x_A and x_B are the concentrations of the two constituents in the alloy.

The CPA and the CCPA that we have introduced here are *exactly* the existing CPA and CCPA, based on various techniques. However, we have expressed the same ideas in a more general form. If we expressed the equations (1) and (2) with a *tight-binding* basis, we would regenerate the standard tight-binding equations. For example, for a *tight-binding* basis the cluster version of (2) leads to the CCPA equation based on the *augmented-space* technique (Mookerjee and Bardhan 1989). Again, if we have muffin-tin, spherically symmetric potentials, and we expand our wavefunctions and Green functions in spherical harmonics, we recover the standard KKR CPA and KKR CCPA. Our formulation, however, is very general. A general form of the potential may be used in the cluster, with arbitrary basis functions. Furthermore, the choice of the surface S is itself quite
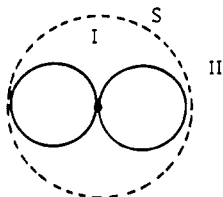

Figure 1. The pair potential cluster and its enclosing spherical interface.

general and need not necessarily follow an equipotential curve. This has been discussed in some detail in an earlier communication (Mookerjee and Bardhan 1989).

In our earlier paper we examined several model cases in which a *single* potential was included in I. In this paper we shall examine the effect of taking *two* potentials in I. Our eventual aim is to estimate the *pair potentials* as one of the chief elements in studying order–disorder transitions in alloys (de Fontaine 1987). We believe that since a pair potential is intrinsically a *two-site* property, a cluster effective-medium approach should give a more accurate picture than an essentially *single-site* mean-field approximation such as the CPA. Accuracy is one of the essential features when one is estimating free energy, if one is to obtain physically significant phase diagrams.

A fully fledged muffin-tin version of the coherent potential leads to

$$G(r, r') = C \sum_L \sum_{L'} [J_l(r_<) - (J_l'(r_S)/H_l'(r_S))] H_l(r_>) Q_{LL'}^{nm}(r_>) Y_L(\hat{r}) Y_{L'}(\hat{r}') \tag{3}$$

where $Q_{LL'}^{nm}(r) = T_{LL'}^{nm}(E) J_l(r) - \delta_{nm} \delta_{LL'} H_l(r)$, **T** being the path operator defined by $(\tau_{coh}^{-1} - \mathbf{B})^{-1}$, τ_{coh} being the *t*-matrix for scattering from a single muffin-tin coherent potential, and **B** the structure factor for the given lattice. J_l and H_l are the regular and irregular solutions for a single muffin-tin coherent potential centred at R_n.

If we take a *jellium* version of the above, and take V_{coh} to be independent of r, but still strongly energy dependent, then the expression is simplified somewhat, at the cost of losing some of the structure arising out of the lattice.

$$G(r, r') = (-i\kappa/4\pi)\Sigma [j_l(\kappa r_<) - (j_l'(\kappa r_S)/h_l'(\kappa r_S))] h_l(\kappa r_>) Y_L(\hat{r}) Y_{L'}(\hat{r}')$$

where j_l and h_l are the spherical Bessel and Neumann functions and $\kappa^2 = 2(E - V_{coh})$.

We shall concentrate first on this simplified model. We shall choose I to be a sphere of radius r_S and within it a pair of muffin-tin potentials in spheres of radii $r_0 = r_S$. The potentials themselves we shall choose to be of the form V/r where V takes the values V_A and V_B with probabilities x_A and x_B respectively. The basis in I will be two s-like functions centred at the two muffin-tin centres r_1 and r_2 (figure 1): $\chi_1(r) = \exp(-|r - r_1|)$ and $\chi_2(r) = \exp(-|r - r_2|)$, with respect to which the Hamiltonian $\mathcal{H}'$ has the 2×2 matrix representation with elements

$$\mathcal{H}_{11} = T + T_S - V_1 I_1 - V_2 I_3 + P(1/r_S - i\kappa)$$

$$\mathcal{H}_{22} = T + T_S - V_2 I_1 - V_1 I_3 + P(1/r_S - i\kappa)$$

$$\mathcal{H}_{12} = T' + T_S' - (V_1 + V_2) I_2 + P(1/r_S - i\kappa) = \mathcal{H}_{21} \tag{4}$$

where

$$T = -\tfrac{1}{4} \int_0^{r_S} \int_{-1}^1 dr \, dt \, r^2 (1 - 2/r_1) e^{-2r_1}$$

$$T' = -\tfrac{1}{4} \int_0^{r_S} \int_{-1}^1 dr \, dt \, r^2 (1 - 2/r_1) e^{-r_1 - r_2}$$

$$T_S = -\tfrac{1}{4} r_S^1 \int_{-1}^1 dt \, (\partial r_1/\partial r)_S e^{-2r_{1S}}$$

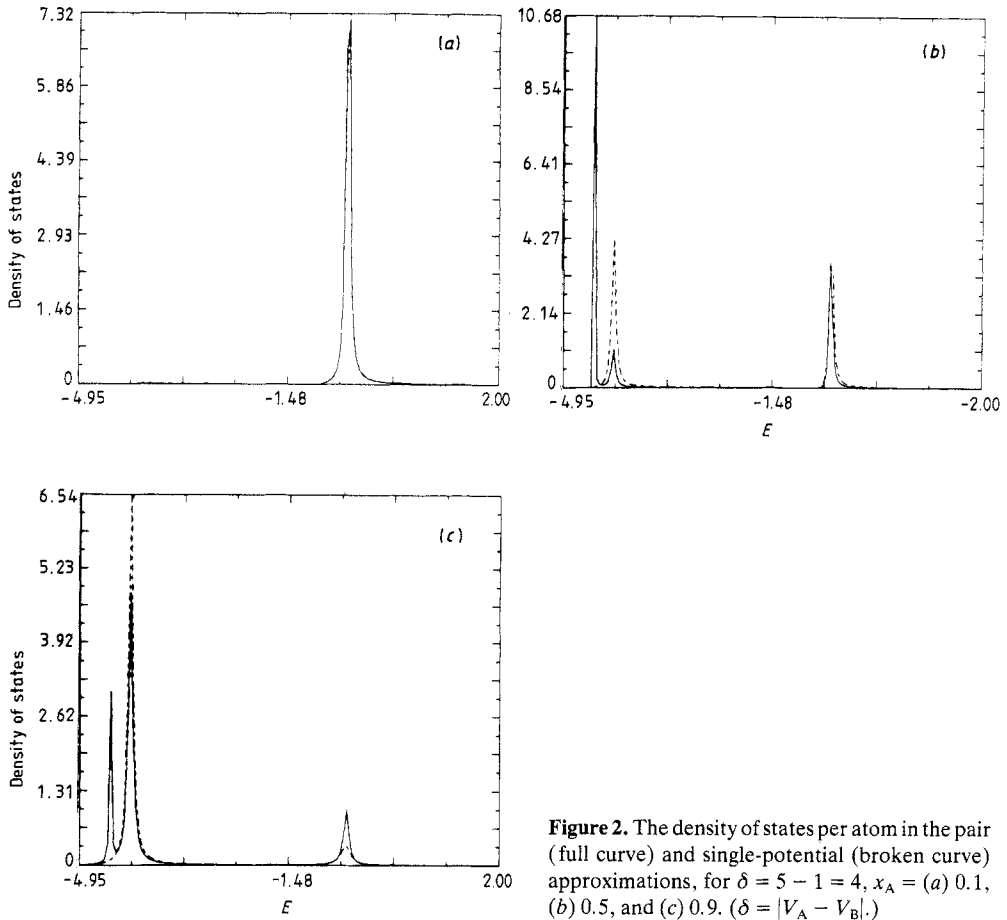$$T_S' = -\tfrac{1}{4} r_S^2 \int_{-1}^1 dt \, (\partial r_1/\partial r)_S e^{-r_{1S} - r_{2S}}$$

Figure 2. The density of states per atom in the pair (full curve) and single-potential (broken curve) approximations, for $\delta = 5 - 1 = 4$, $x_A = (a)$ 0.1, (b) 0.5, and (c) 0.9. $(\delta = |V_A - V_B|.)$

$$r_1^2 = r^2 + r_0^2 - 2rr_0t \qquad r_2^2 = r^2 + r_0^2 + 2rr_0t$$

$$I_1 = \tfrac{1}{4} - (\tfrac{1}{4} + r_0/2)\,e^{-2r_0}$$

$$I_2 = (e^{-2r_0}/4r_0)[3r_0/2 - \tfrac{3}{4} + (3r_0/2 + \tfrac{3}{4})\,e^{-2r_0}]$$

$$I_3 = (e^{-4r_0}/8r_0)[(2r_0 + 1)(\cosh(2r_0) - 1) - r_0\sinh(2r_0)]$$

$$P = (r_S^2/8)\left(\int_{-1}^{1} e^{-r_{1S}}\,dt\right)^2$$

$$\mathbb{S}_{11} = \tfrac{1}{2}\int_0^{r_S}\int_{-1}^{1} dr\,dt\,r^2\,e^{-2r_1} = \mathbb{S}_{22}$$

$$\mathbb{S}_{12} = \tfrac{1}{2}\int_0^{r_S}\int_{-1}^{1} dr\,dt\,r^2\,e^{-r_1-r_2} = \mathbb{S}_{21}.$$

Equation (2) for the coherent potential reduces to a cubic equation for κ and the complex
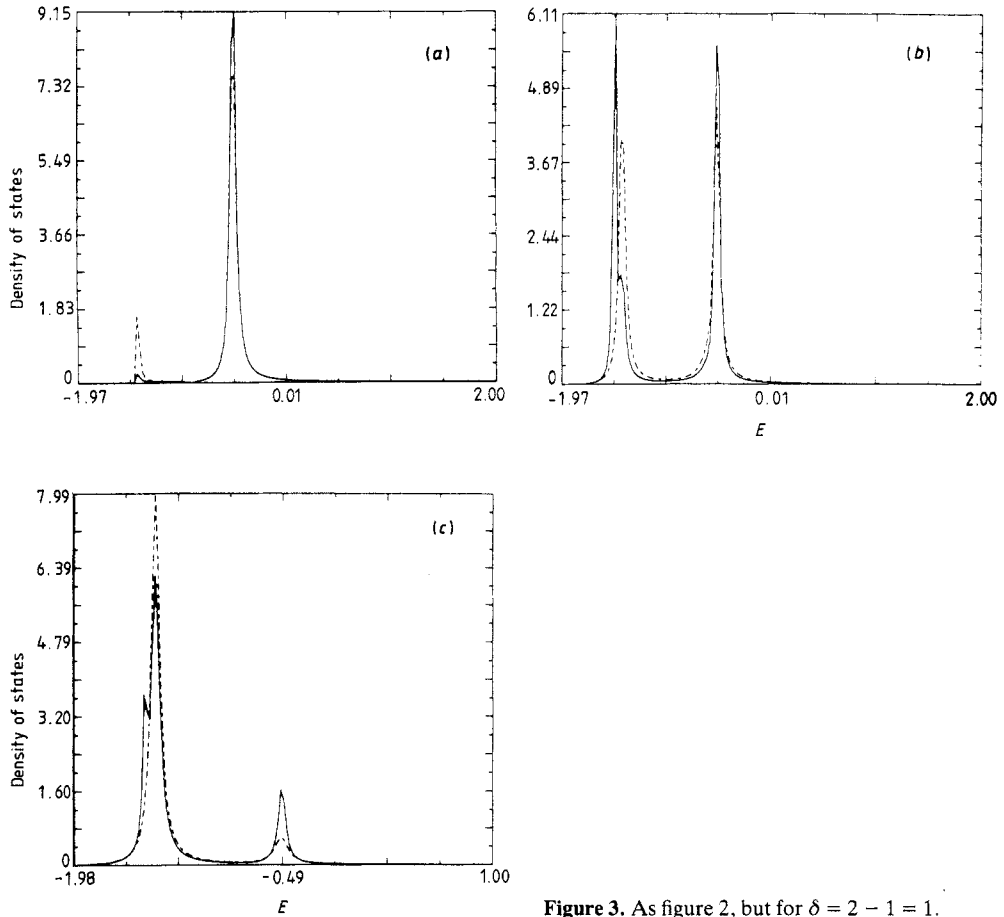
Figure 3. As figure 2, but for $\delta = 2 - 1 = 1$.

root with the *herglotz analytic property* is the correct choice for the problem. The Green function in this basis is a 2×2 matrix given by $\mathbb{G} = (\mathcal{H} - E\mathbb{S})^{-1}$ and the density of states per atom is given by

$$n(E) = -(1/2\pi) \operatorname{Im} \operatorname{Tr} \left(\mathbb{S}\mathbb{G}(E - i0) \right). \tag{5}$$

It is interesting to note that the problem is very similar to the problem of a hydrogen-like molecule in I immersed in a coherent medium in II. The various integrals involved in (4) are familiar two-centre integrals in the finite subspace I. If we had taken larger clusters, then the problem would have involved multi-centre integrals; the method of calculation of these has been developed well in molecular chemistry.

Figures 2–4 show the density of states for the two-potential clusters, as compared with the earlier one-potential calculations reported in an earlier paper (Mookerjee and Bardhan 1989). The parameters chosen are the same as reported in that earlier paper with $|V_A - V_B| = 4, 1$ and 0.2 while $x_A = 0.1, 0.5$ and 0.9. The principal new feature is the splitting of the lower-energy peak into bonding and anti-bonding structures. There is no such split in the higher-energy peak, probably because the spread in this energy regime caused by the large imaginary part in the surface potential related to K causes
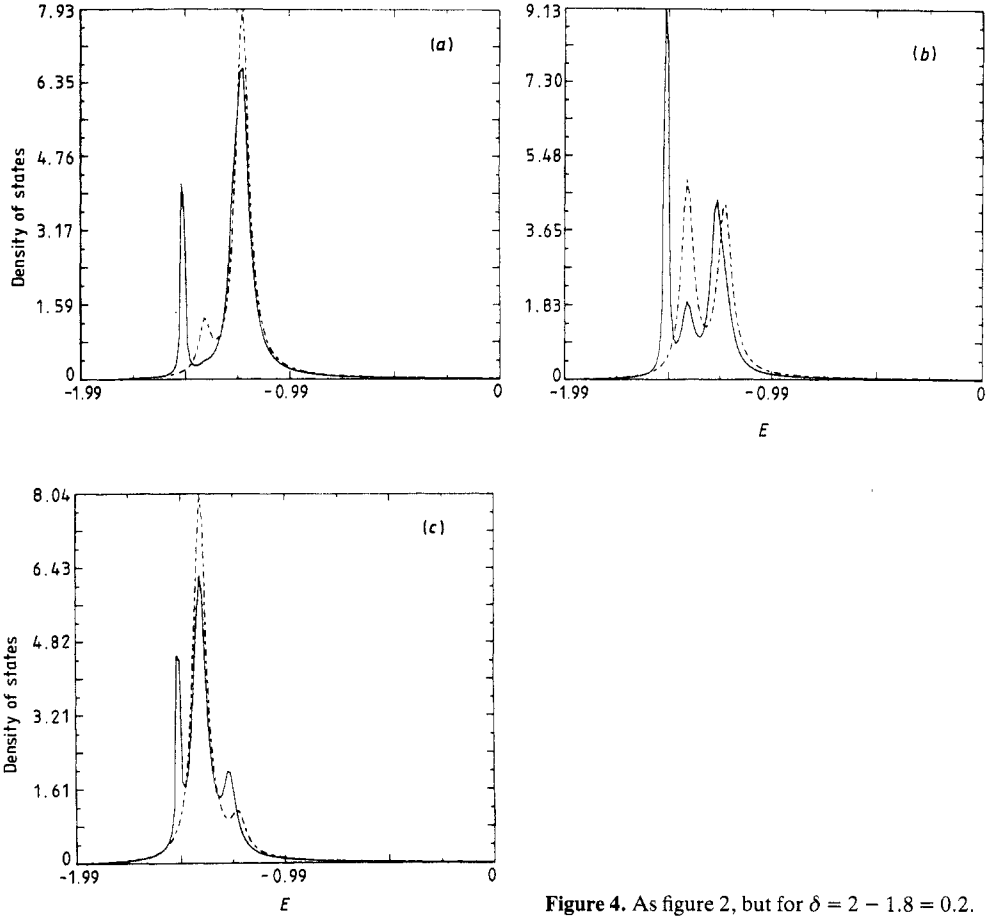
Figure 4. As figure 2, but for $\delta = 2 - 1.8 = 0.2$.

overlap and the two peaks are not resolved. If we had looked at a basis with d-like symmetry (as in the earlier paper), the structures would have been sharper and we would have expected considerable new structure to appear when we chose a larger cluster enveloped in I.

For one of the cases we have also derived the pair potential from the generalised phase shift $Z(E)$

$$E_2 = \left\langle -\tfrac{1}{4} \int_{-\infty}^{E_F} \text{Im } Z(E) \, \mathrm{d}E \right\rangle_\sigma \tag{6}$$

where $Z(E) = (-1/\pi) \ln \det(\mathbb{G}_{AA}\mathbb{G}_{BB}/\mathbb{G}_{AB}\mathbb{G}_{BA})$ $\mathbb{G}_{pq}$ is the Green function in which the potentials in the space I have the specific configuration pq (AA, BB or AB).

This form of the pair potential E_2, in terms of the generalised phase shifts, has been introduced recently by Barera *et al* (1988). It is based on the generalised perturbation method of Ducastelle and Gautier (1976). The details of the derivation have been discussed by Ducastelle and Gautier (1976) and de Fontaine (1987).
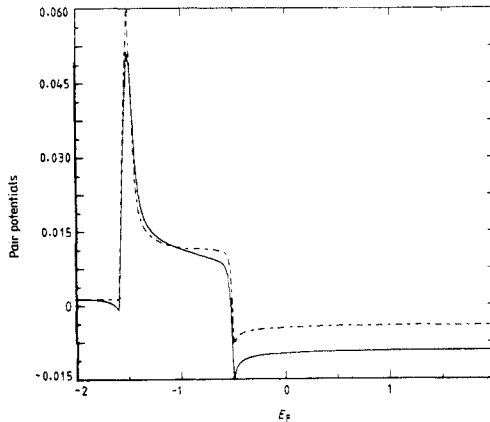
Figure 5. The pair potential versus the position of E_F for the same case as for figure 3.

Figure 5 shows the pair potential as a function of the Fermi energy, which itself varies with the band filling according to

$$\int_{-\infty}^{E_F} n(E)\, dE = x_A n_A + x_B n_B \qquad n(E) = \frac{-1}{\pi} \mathrm{Im} \int d\, r\, G(r, r', E + i\delta). \tag{7}$$

This figure is to be compared with the figure given by Barera *et al* (1988). Their work was on a FCC lattice, whereas we have taken a jellium background. While this would have quite a noticeable effect on the detailed structure of the density of states, the pair potential, being an integrated quantity, is not expected to show much variation with individual lattice structure. This is clear from the comparison of the two figures. Qualitatively the pair potential of Barera *et al* (1988) is very similar to ours with the characteristic peak and regions of negative E_2. The characteristic shape tells us that for the given parameters of the model ($x_A = 0.5$, $V_A = -2.0$, $V_B = -1.0$ units), for a given range of band filling such that the Fermi energy lies in the range (-1.5 to -0.5), the AB type of alloying is favoured. It does not tell us whether the alloy will be ordered or random. That can only be decided after we have compared the Gibbs free energies of the two orderings calculated from the pair potentials. There is also a range of band filling, with the Fermi energy lying above -0.5 units when the pair potential goes negative and AA- or BB-type bonding is favoured, leading to phase separation. The shape of the pair potential, of course, depends upon the parameters of the model. However, the characteristic shape with a region favouring AB-type bonding and another favouring phase separation seems to be a common feature.

The single-potential CPA cannot be used to estimate the pair potential accurately, as that is essentially a two-potential property. For the given parameters of our model the 2CPA consistently predicts a favourable phase separation when compared with the 1CPA results.

Our aim is the application of this formalism to estimate the effective cluster interactions in alloy systems, in order to tackle from first principles the problem of predicting temperature–concentration phase diagrams in these systems. The formalism proposed is general enough and tractable enough for this purpose.

Acknowledgments

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