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1991 J. Phys.: Condens. Matter 3 9651

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## A variational approach to cluster approximations in the theory of electronic structure of disordered alloys

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Received 25 July 1991

**Abstract.** Cluster generalization of the CPA method, based on the variational calculation of the alloy thermodynamic potential, is considered. Various possible choices of the variational parameters are discussed. One of them leads to an approximation that is analogous to the Bethe approximation for the Ising model. The technique developed is applied to the calculation of the density of states in the  $\text{Ni}_{1-c}\text{Cu}_c$  alloy by the LMTO-ASA method.

### 1. Introduction

The CPA method for alloy electronic structure calculations [1] appears at present to be the most reliable one. The method is widely used and numerous applications to various alloys are known, including the full self-consistent KKR-CPA density of states calculations that are in good agreement with experiment (see for example [2]). In the original papers it was already pointed out that this method is a version of the mean-field method used, for example, for the investigation of the Ising model. At the given energy  $\varepsilon$  the expansion parameter is proportional to  $\zeta \sim c_a c_b \Delta U / n\varepsilon$ , where  $n$  is the number of the nearest neighbours,  $c_a$  and  $c_b$  are the concentrations of alloys constituents, and  $\Delta U$  is the difference between their potentials. (See for example [1].) In our case this mean field  $\Sigma_0(\varepsilon)$  is the self-energy of the effective Green function  $\tilde{G}_0(\varepsilon) = \text{Sp}[\varepsilon - \varepsilon_k - \Sigma_0(\varepsilon)]^{-1}$ . Similarly to the Ising model calculations this mean-field parameter can be found either from the condition of the self-consistency (in our case it is the coincidence of the effective  $\tilde{G}_0(\varepsilon)$  and the averaged Green function  $\langle G_0(\varepsilon) \rangle$ ) or from the condition of the thermodynamic potential (TP)  $\Omega$  minimum. In the latter case TP is considered to be a functional of  $\Sigma_0(\varepsilon)$ . The equivalence of both approaches was proved by Lloyd and Best [3].

The cluster generalization of the CPA method was also proposed in [3]. It was suggested that the averaged TP  $\Omega$ , calculated for the system with definite potentials  $U_i$  in sites  $i_1, i_2, \dots, i_n$  of the lattice, and with the mean potentials  $\Sigma_0(\varepsilon)$  in other sites, should be minimized with respect to these  $\Sigma_0(\varepsilon)$ . Such an approach is similar to that for the Ising model when the interaction  $J$  between two lattice sites is taken into account directly, and interactions with the other sites are taken into account via the field  $\varphi \sim J(n-1)\sigma$  with the further  $\Omega$  minimization over the mean spin  $\sigma$ . But it is known that such an approach usually only slightly modifies the one-site mean-field results and in the cases when strong correlations between the neighbouring atoms

should be taken into account, another approach—the Bethe approach—should be used. The cluster variational method (CVM), which is the generalization of the Bethe and Kikuchi approaches, is widely used in the theory of substitutional alloys ordering on the lattice (see for example [4]). The simplified form of the CVM—the cluster field method (CFM)—was proposed in [5]. The necessity of the analogous approach for the disordered alloy electronic calculations was emphasized in [6].

The present work is devoted to the realization of such an approach, i.e. the generalization of the CPA method in the spirit of the CVM approach. In section 2 corresponding cluster fields are discussed. There are a number of cluster CPA generalizations (see for example [7–10] and the literature cited there) but the self-consistency equations are not, as a rule, the consequence of any variational principle differing at this point from the equations obtained below. As a consequence the proposed earlier conditions of the self-consistency are a bit arbitrary. For example the Green function at the central cluster site or at its boundary is equated to the Green function of the medium. More elaborate conditions also exist. The problem of the choice of the proper equations appears to be closely related to the analyticity problem, i.e. to the behaviour of the Green function in the complex  $\varepsilon$  plane. Only in some cases [7, 10] was the Green function proved to possess the Herglotz property. In other cases it evidently violates it and for several approaches numerical investigations show that the Green function has satisfactory behaviour though this has not been proved analytically. The discussion of the equations arising in the variational approach (section 2) shows that a number of parameters should be included to restore the equality of the density of states  $g_G(\mu)$  obtained via the Green function with that obtained via the TP  $\Omega$  differentiation ( $g_\Omega(\mu)$ ). This identity is valid for exact  $\Omega$  and exact averaged Green function and is violated when arbitrary self-consistent equations are imposed. Such an inequality usually does not permit us to consider one of these  $g(\mu)$  as having a physical meaning and it may be the underlying mechanism of the analyticity violation.

The variational principle automatically creates proper equations and the problem now shifts to the choice of adequate variational parameters. It is known that in the case of the many-body theory the variational principle with the self-energy  $\Sigma(\varepsilon, \mathbf{k})$  as a variational parameter really brings on the equality of the one-electron properties calculated thermodynamically and through the Green function [11]. It will be shown below that the CPA can be rewritten in the form corresponding to such an approach and it is known that the CPA Green function has the Herglotz property. So we can hope that the variational approach with the number of parameters sufficient for the maintenance of the thermodynamic identities will give a Green function with the true analyticity properties. Of course such a statement can hardly be proved in general as the experience of the CFM [5] calculations shows that in large clusters it is always possible to make the wrong choice. For the two-site cluster in  $\text{Ni}_{1-c}\text{Cu}_c$  alloys we did not notice numerically any difficulties with the analyticity.

Generally the variational parameter, i.e. the effective medium description, can be introduced in several ways and in section 3 a similar approach is carried out with the variational parameters included in the free term of the integral equation for the wave function with the kernel  $G_\gamma(r)$ . The  $G_\gamma(r)$  Green function corresponds to the solution of the Schrödinger equation increasing along a certain direction  $\gamma$  [13]. Such an approach is close to the transfer matrix approach widely used in the one-dimensional case (see for example [14]).

For the variant which is the analogue of the CFM [5] and appears to be the simplest one, the comparison of results for the LMTO-ASA-CPA method with that in the LMTO-

ASA cluster approximation was made for the  $\text{Ni}_{1-c}\text{Cu}_c$  alloys. This alloy is thoroughly investigated by various methods, in particular by the full KKR-CPA method [2], and can be used for testing new approaches. The cluster approximation in this case gives results which appear to be slightly closer to the experiment than the CPA ones, but the differences turn out to be negligible. We believe that the use of cluster approximations is significant for the investigations of the influence of the alloy short-order on its electronic structure [10] or for the configurational interaction calculations when the consistency of the effective medium and of the cluster are important.

The generalizations of the main equations with the electron-electron interaction included in the framework of the density functional (DF) method are also discussed in section 2. The variational calculations of vertex corrections to the interaction of the electron with the impurity in the alloy are described in the appendix. For clarity of presentation we confine ourselves only to the case of the tight-binding Hamiltonian with diagonal disorder, but the generalization for the cases of LMTO or KKR methods appears to be evident.

## 2. Cluster field method

The model of the binary substitutional alloy described by the tight-binding Hamiltonian  $H$  with the diagonal disorder for  $s$ ,  $p$  and  $d$  electrons and with the concentration of the alloy constituents  $c_a$  and  $c_b$  will be considered below. Besides, such an approach is equivalent to the LMTO-ASA approach for the case when the bandwidths of both constituents are equal [15].

The one-electron TP  $\Omega_e$  for the system with potentials  $U_i$  in lattice sites  $i$  can be expressed via the exact Green function  $G$  as an integral over the contour in the complex plane  $z$  [14]:

$$\Omega_e = \frac{1}{2\pi i} \text{Tr} \int_C \left\{ \sum_{\mathbf{k}} \ln(-G^0) dz - \sum_i \ln(1 - \Delta U_{ia} G^0) dz - \sum_{i < j} [\ln(1 - \Delta U_{ia} G^0 - \Delta U_{ja} G^0) - \ln(1 - \Delta U_{ia} G^0) - \ln(1 - \Delta U_{ja} G^0)] dz - \dots \right\} \quad (1)$$

where  $G^0(z)$  corresponds to the Hamiltonian of the  $a$ -component host lattice and  $\Delta U_{ia} = U_i - U_a$ .  $\text{Tr}$  means the summation over electron degrees of freedom. Contour  $C$  is shown in figure 1(a). It embraces the cut along the real axis, where eigenvalues of the Hamiltonian  $H$  are contained. If the contour crosses the real axis at the point  $\mu$  (figure 1(b)), then equation (1) corresponds to the TP of the system with the  $N = N(\mu)$  electrons [3]. As the functions  $G^+$  and  $G^-$  are analytical ones in the upper and lower semiplanes respectively, the contour can be arbitrarily deformed in these semiplanes (figure 1(c)). Only local variational parameters, i.e. those depending on the energy  $z$  at the point of calculation, will be introduced below and therefore the detailed form of the contour is unimportant. After averaging (1) over a random distribution on the lattice of the atoms of type  $a$  and  $b$ , we shall obtain the series in concentration  $c$ , which is the  $\Omega_e$  virial expansion [14]. It is convenient to count the potential from its mean value  $\bar{U} = \langle U_i \rangle = c_a U_a + c_b U_b$  and to introduce the effective mean field

$\Sigma(z, \mathbf{k}) = \sum_{\mathbf{R}} [\Sigma_{\mathbf{R}}(z) \exp(i\mathbf{k} \cdot \mathbf{R})]$  in the definition of the medium effective Green function

$$\tilde{G}(z, \mathbf{k}) = (z - H_{\mathbf{k}} - \Sigma(z, \mathbf{k}) - \bar{U})^{-1} \quad \tilde{G}_{\mathbf{R}}(z) = \sum_{\mathbf{k}} \tilde{G}(z, \mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{R}). \quad (2)$$

Adding and subtracting  $\Sigma_{\mathbf{R}}(\epsilon)$  in various clusters we can rewrite (1) in the form

$$\Omega_e = \Omega_0 + \sum_i \Omega_i + \sum_{i < j} (\Omega_{ij} - \Omega_i - \Omega_j) + \dots$$

$$\Omega_0 = \frac{1}{2\pi i} \text{Tr} \int_C \sum_{\mathbf{k}} \ln[-\tilde{G}(z, \mathbf{k})] dz \quad \Omega_i = -\frac{1}{2\pi i} \text{Tr} \int_C \ln[1 - (V_i - \Sigma_0)\tilde{G}] dz \quad (3)$$

$$\Omega_{ij} = -\frac{1}{2\pi i} \text{Tr} \int_C \ln [\delta_{i_1 i_2} - (V_{i_1} - \Sigma_{i_1 i_2})\tilde{G}_{i_1 i_2}] dz$$

where  $i_1, i_2$  are  $i$  or  $j$ , and  $V_i = U_i - \bar{U}$ . Subsequent terms of the equation (3) have a cumulant structure and represent contributions to  $\Omega_e$  from  $n$ -site clusters.

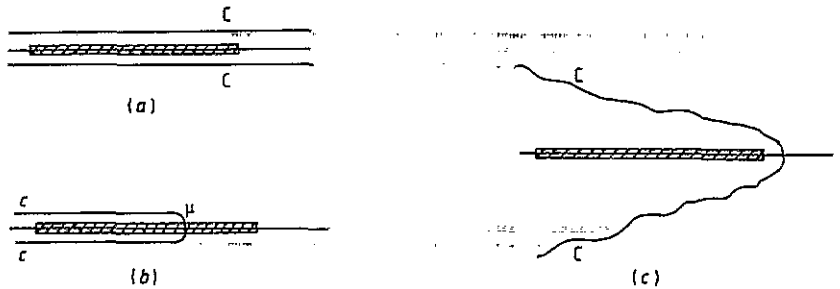


Figure 1. Contours of integration in the expression for  $\Omega$ .

Averaging (3) and truncating the series, one gets an approximated  $\Omega_e$  functional depending on  $\Sigma_{\mathbf{R}}(\epsilon)$  which can be treated as a variational parameter. It is worth noting that the additions and the subtractions of  $\Sigma_{\mathbf{R}}(\epsilon)$  do not change the Hamiltonian  $H$  and are identity transformations until the series is truncated. With only one-site cluster terms being held in (3), the corresponding equation has the form [3]:

$$\begin{aligned} \Omega_e &= \Omega_0 + N\langle \Omega_i \rangle \\ \tilde{G}(z, \mathbf{k}) &= (z - H_{\mathbf{k}} - \tilde{\Sigma}_0 - \bar{U})^{-1} \\ \tilde{G}_0 &= \sum_{\mathbf{k}} \tilde{G}(z, \mathbf{k}). \end{aligned} \quad (4)$$

In this case only a mean field  $\Sigma_0(\epsilon)$  at  $R = 0$  can be included. Minimizing (4) over  $\Sigma_0(z)$  under the condition that this minimum is valid for any deformation of the integration contour at point  $z$ , we get

$$\tilde{G}_0 \delta \Sigma_0 + \left\langle \frac{V_i - \Sigma_0}{1 - (V_i - \Sigma_0)G_0} \delta \tilde{G}_0 - \frac{\tilde{G}_0}{1 - (V_i - \Sigma_0)G_0} \delta \Sigma_0 \right\rangle = 0. \quad (5)$$

This condition can be also rewritten as  $\langle T_i \rangle (\delta \tilde{G}_0 - \tilde{G}_0 \delta \Sigma_0 \tilde{G}_0) = 0$ , where the one-site scattering matrix  $T_i$  is introduced. Thus we get the usual CPA equation [3]:

$$T_i = \frac{V_i - \Sigma_0}{1 - (V_i - \Sigma_0)G_0} \quad \langle T_i \rangle = 0. \tag{6}$$

It is worth noting that due to this condition, the densities of states  $g(\epsilon)$ , calculated through Green function and through differentiating TP  $\Omega_e$  over  $\mu$ , coincide [11, 12]:

$$n(\mu) = -\frac{\text{Tr Disc } \tilde{G}_0(\mu)}{2\pi i} \tag{7}$$

where  $\text{Disc } F(z) = F(z + i0) - F(z - i0)$ . The equation (4) can be rewritten in another form, which immediately reveals the coincidence of this  $\Omega_e$  with the functional introduced in [11] for many-body systems. The equation (6) is equivalent to  $\Sigma_0(\epsilon) = \langle V_i / [1 - (V_i - \Sigma_0)\tilde{G}_0] \rangle$ . With this  $\Sigma_0(\epsilon)$  the sum  $\Phi$  of all the skeleton diagrams determined by the condition  $\delta\Phi/\delta G = \Sigma(\epsilon)$  can be expressed as  $\Phi[G] = \text{Tr} \{ \langle \Sigma_0 \tilde{G}_0 - \ln [1 - (V_i - \Sigma_0)\tilde{G}_0] \rangle \}$ . We see that (4) has the form of the Luttinger-Ward functional

$$\Omega_e = \frac{1}{2\pi i} \text{Tr} \left\{ \int_C \sum_k \left[ \ln(-\tilde{G}) - \Sigma_0 \tilde{G} \right] \right\} dz + \Phi[\tilde{G}]. \tag{8}$$

Thus it is proved that the  $\Sigma_R(\epsilon)$  variable introduced in (8) as an exact averaged Green function self-energy has the meaning of an effective field (4) acting on an electron.

This duality can be useful for the generalization of the cluster expansion (3) for the  $n$ -site cluster case. It should be noted that instead of including variational parameters in the Green function self-energy one can include them as effective fields in the  $\Omega_e$  expansion. Similarly to the CFM in the theory of alloys ordering [5], we introduce fields  $\Psi$ , which are not simply added or subtracted in the initial Hamiltonian, but which are added and subtracted in various terms of the virial expansion for  $\Omega_e$  in such a way that their sum in the averaged Hamiltonian is zero [5]. So apart from directly including  $\Sigma(\epsilon)$  in the Hamiltonian, which is natural for the case when  $\Sigma(\epsilon)$  is interpreted as the self-energy, we can introduce the field  $\Psi_R$  in the expansion (3) so that the sum over all clusters disappears.

For the two-site cluster we introduce two sorts of parameters:  $\Sigma_R$  and  $\Psi_R$ .  $\Sigma_0$  and  $\Sigma_R$  are added and subtracted in the Hamiltonian and are consequently introduced into the Green function  $G_R(\epsilon)$ . The one-site parameters  $\Psi_R$  in the one-site cluster yield the mean field  $\Psi = \Sigma \Psi_R$  and in the two-site cluster with sites  $R_i$  and  $R_i + R$  give the field  $\Psi - \Psi_R$  at the  $R_i$  site. We get from (3):

$$\begin{aligned} \Omega_e &= \Omega_0 + \sum_i \langle \Omega_i \rangle + \frac{1}{2} \sum_{ij} \langle (\Omega_{ij} - \Omega_i - \Omega_j) \rangle \\ \Omega_i &= -\frac{1}{2\pi i} \text{Tr} \int_C \ln(1 - (V_i - \tilde{\Sigma}_0 + \Psi)\tilde{G}_0) dz \\ \Omega_{ij} &= -\frac{1}{2\pi i} \text{Tr} \int_C \ln \left( \begin{array}{c} 1 - (V_i - \tilde{\Sigma}_0 + \Psi - \Psi_R)\tilde{G}_0 \\ + \Sigma_{-R}\tilde{G}_R \end{array} \quad \begin{array}{c} + \Sigma_R\tilde{G}_{-R} \\ 1 - (V_j - \tilde{\Sigma}_0 + \Psi - \Psi_{-R})\tilde{G}_0 \end{array} \right) dz \end{aligned} \tag{9}$$

where  $\Omega_0$  and  $\tilde{G}_R(\epsilon)$  are as in (2) and (3). We want to emphasize once more that it is not possible to introduce variational parameters  $\Psi_R$  at the level of the Green-function self-energy, and they must be included directly in TP  $\Omega_e$ . Due to the non-commutativity of various cluster Hamiltonians the introduction of such fields can cause non-trivial variations in the form of the  $g(\epsilon)$  function.

To find these fields from the condition of the  $\Omega_e$  minimum it is convenient to introduce the Lagrange multiplier  $\eta$  and to vary  $\Omega_e - \eta(\Psi - \sum_R \Psi_R)$  with respect to  $\Psi$  and  $\Psi_R$  independently. Thus we get

$$\langle G_{ii}^1 \rangle = \langle G_{ii}^2 \rangle \tag{10}$$

where  $G_R^{1,2}(\epsilon)$  is the Green function defined with potentials  $U_i$  either in one-site or two-site clusters. Varying (9) over  $\Sigma_0$  and  $\Sigma_R$  we get correspondingly

$$\sum_i \langle T_i \rangle K_i + \frac{1}{2} \sum_{ij} \langle T_{ij} \rangle K_{ij} = 0 \tag{11a}$$

$$\sum_i \langle T_{ii+R} \rangle K_{ii+R} = 0 \tag{11b}$$

$$K_i = \tilde{G}_{ii} \tilde{G}_{ii} + \left. \frac{\partial \tilde{G}_{ii}}{\partial z} \right|_{\Sigma} \quad K_{ij} = \sum_{k=i,j} \tilde{G}_{ki} \tilde{G}_{ik} + \left. \frac{\partial \tilde{G}_{ij}}{\partial z} \right|_{\Sigma} \tag{11c}$$

Finally let us write down the expression for the density of states  $n(\mu) = -\frac{\partial^2 \Omega_e}{\partial^2 \mu}$

$$\begin{aligned} n(\mu) &= -\frac{\text{Disc}}{2\pi i} \left[ \sum_k \tilde{G}(\mu, k) - \sum_i \langle T_i^1 \rangle D_i - \frac{1}{2} \sum_{ij} \langle T_{ij}^2 \rangle D_{ij} - T_i^1 D_i - T_j^1 D_j \right] \\ D_i &= -\sum_k \tilde{G}(\mu, k) \left( 1 + \frac{\partial \Sigma(\mu, k)}{\partial \mu} \right) \tilde{G}(\mu, k) \\ D_{ij} &= -\sum_k \exp^{ik(R_i - R_j)} \tilde{G}(\mu, k) \left( 1 + \frac{\partial \Sigma(\mu, k)}{\partial \mu} \right) \tilde{G}(\mu, k). \end{aligned} \tag{12}$$

Let us trace the influence of various fields and approximations on the  $n(\mu)$  value. Without variational parameters the equation (12) gives the expression for  $n(\mu)$  in the usual T-matrix approximation:

$$\begin{aligned} n(\mu) &= -\frac{\text{Disc}}{2\pi i} \text{Sp} \left[ G^0 + G^0 \langle T_i^1 \rangle G^0 \right. \\ &\quad \left. + \frac{1}{2} \sum_R (G^0 \langle T_{ii+R}^2 \rangle G^0 - G^0 \langle T_i^1 \rangle G^0 - G^0 \langle T_{i+R}^1 \rangle G^0) \right] \end{aligned} \tag{13}$$

Sp in (13) also means summation over the lattice sites not included in the cluster. With the minimization over  $\Sigma_0$ , as was suggested in [3], the joint contribution of (11a) and (11b) causes the replacement of the  $G_R^0(\epsilon)$  Green function by  $\tilde{G}_R(\epsilon)$  in (13), and  $T_i^1, T_{ij}^2$  by scattering matrices corresponding to potentials  $V_i - \Sigma_0$ . Nevertheless  $n(\mu)$  and  $-\frac{\text{Disc}}{2\pi i} \tilde{G}_0$  do not coincide:

$$n(\mu) = -\frac{\text{Disc}}{2\pi i} \text{Sp} \left[ \tilde{G}_0 + \tilde{G}_0 \langle T_i^1 \rangle \tilde{G}_0 + \frac{1}{2} \sum_R (\tilde{G}_{ik} \langle T_{kl}^2 \rangle \tilde{G}_{li} - 2\tilde{G}_0 \langle T_i^1 \rangle \tilde{G}_0) \right]. \tag{14}$$

Now the summation in (14) in contrast with (13) is restricted to the sites  $kl$  belonging to the selected cluster  $ij$  ( $R_j = R_i + R$ ) only.

The introduction of  $\Psi_R$  fields and thus the validity of (10) gives

$$n(\mu) = -\frac{\text{Disc}}{2\pi i} \text{Tr}(\tilde{G}_0 + \tilde{G}_0 \langle T_i^1 \rangle \tilde{G}_0). \quad (15)$$

Finally, introducing  $\Sigma_R$  leads to equation (11b). The whole system of equations (10), (11a-c) has the only zero solution. Thus  $\langle T_i^1 \rangle = \langle T_{ij}^2 \rangle = 0$  and  $n(\mu) = -\text{Disc Tr}(\tilde{G}_0)/(2\pi i)$ .

So we see that the inclusion of the  $\Psi_R$  fields plays an important role ensuring the self-consistent variations of the density in the one- and two-site clusters. In its turn  $\Sigma_0$  improves the convergence of the (1) series, as  $G_R^+(\varepsilon)$  is proportional to  $\exp[i(\varepsilon_k + \Sigma_0)^{1/2} R]$  and it exponentially vanishes when  $\Sigma$  has an imaginary part. Finally, introduction of  $\Sigma_R$  makes the averaged scattering matrix  $\langle T_{ij} \rangle$  equal to zero, and in turn causes the vanishing of the averaged electron density around cluster sites. The disappearance of  $\Delta\rho$  around the cluster is important for the self-consistent configurational interaction calculations.

For the  $n$ -site clusters new additional parameters can be included, not only of the one-site type such as  $\Psi_R$ , but corresponding to multiple scattering at several sites, in close analogy with that of CVM [5]. As an example of an introduction of such effective non-local interactions, we discuss in the appendix the  $\Gamma(R_1, R_2, R_3)$  vertex calculations for the scattering of an electron on the impurity in an alloy.

Let us mention the necessary modifications for the incorporation the electron-electron interaction into our scheme. In the DF method the potential  $U_i$  at every lattice site  $i$  should now depend on the density  $\rho_i$  at this and other lattice sites. We add the electron-electron 'double-counting' terms  $\Omega_{ee}$  to  $\Omega_e$ :

$$\Omega_{ee} = \text{Tr} \left[ \left\langle \sum_i (\Phi_{ee}[\rho_i] - V_i \rho_i) + \sum_{i < j} [(\Phi_{ee}[\rho_{ij}] - V_{ij} \rho_{ij}) - 2(\Phi_{ee}[\rho_i] - V_i \rho_i)] \right\rangle \right] \quad (16)$$

where  $\rho_i(r)$  and  $\rho_{ij}(r)$  are respectively the electron density in the one-site and two-site  $ij$  clusters,  $\Phi_{ee}[\rho]$  in the local density approximation (LDA) for the exchange and the correlation terms is

$$\frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + \Phi_{xc}(\rho(r)) \quad V_{ee}[\rho] = \int \frac{\rho(r')}{|r-r'|} dr' + \mu_{xc}(\rho(r))$$

for the electron-electron potential  $V_{eei} = V_{ee}(\rho_i)$ . The potential  $U_i$  for every cluster contains correspondingly  $V_{eei}$  or  $V_{eeij}$ . Then for the total  $\Omega = \Omega_e + \Omega_{ee}$  the necessary condition  $\delta\Omega/V_{eei} = \delta\Omega/V_{eeij} = 0$  is valid. For the one-site cluster the total CPA energy calculated with the use of (3) and (16) coincides with that found in [16]. For the  $n$ -site cluster it is seen that the condition (10), i.e.  $\rho_i(r) = \rho_{ij}(r)$  is extremely important for the self-consistency of such an approach.

### 3. The cluster embedding method

We believe that the virial expansion of TP  $\Omega_e$  is the flexible technique for the introduction of various variational parameters. In section 2 such parameters were introduced



as effective fields, acting on and between lattice sites. But the consideration of the transfer matrix method in the one-dimension case [14] shows that it is possible to introduce variational parameters corresponding to variations of the wave function boundary conditions. Such an approach, which can be called the cluster embedding method, is discussed in this section.

Let us start from the integral form of the Schrödinger equation

$$\Psi_{\mathbf{R}} = \Psi_{\mathbf{R}}^0 + \sum_{\mathbf{R}'} G_0^+(\mathbf{R} - \mathbf{R}') V_{\mathbf{R}'} \Psi_{\mathbf{R}'} \quad (17)$$

with the potential  $V_i$ , existing in  $n$  lattice sites  $i_1, \dots, i_n$ . Now the exclusion of  $V_n$  in (17), i.e. the reduction of the equation to  $n - 1$  sites with the other sites considered as 'host-sites', results in changing the free term  $\Psi_{\mathbf{R}}^0$  and changing the kernel function  $G^+(\mathbf{R} - \mathbf{R}')$ . Thus the direct averaging of (17) results only in the simplest approximations such as the average  $t$ -matrix approximation. For more elaborate approximations the parametrization of the kernel  $G^+$  should be done, thus returning us to the section 2 formulae. Another way involves a proper choice of the kernel from the very beginning.

To explain further formulae let us temporarily consider a one-dimensional continuous chain with the potentials  $U_i(x - x_i)$ . In the one-dimensional case one can choose functions  $G^>, G^< = -\Theta(\pm r) \sin(kr)/k$  instead of  $G^+$  [13]. Then the reduction of the  $n$  lattice site would cause only the variation of  $\Psi^0$ , and the kernels  $G^>$  or  $G^<$  would stay the same. In other words using  $G^>$  permits the transformation of the Hermitian matrix  $G^+$  of the linear equation system for  $\Psi_r$  to the upper triangle matrices  $G^>$ . The solution of the system with the triangle matrix can be done by the subsequent exclusion of variables from larger  $r$  to smaller or vice versa. Such solutions in the scattering theory are called the Jost solutions and they contain all the information about the scattering matrix. Representing  $\Psi_r$  in the form

$$\begin{aligned} \Psi_k(r) &= \alpha_k(r) e^{ikr} + \beta_k(r) e^{-ikr} \\ \Psi'_k(r) &= ik[\alpha_k(r) e^{ikr} - \beta_k(r) e^{-ikr}] \end{aligned} \quad (18)$$

we get the linear system for  $\alpha$  and  $\beta$  similar to the variable phase method or embedding method equations [17] and the limit of  $\alpha(r)$  at  $r \rightarrow -\infty$  will coincide with the Jost function [13]. The exact solution of the one-dimensional chain, resulting in the Dayson integral equation for the phase  $\varphi$  probability function  $W(\varphi)$ , uses such a representation [14]. It can be checked that the use of the two nearest neighbours site cluster results in the Dayson equation for the probability  $W(\alpha)$  if the wave function in the boundary points is represented as in (18). An approximate solution can be obtained with constants  $\alpha_k$  and  $\beta_k$ , determined from the  $\Omega_e$  minimum condition.

Let us return to the three-dimensional discrete lattice. In this case there are no Green functions which behave literally as  $G^>$  or  $G^<$ , i.e. proportionally to  $\Theta(\gamma r)$  or  $\Theta(-\gamma r)$  for the arbitrary direction  $\gamma$ . But in the theory of the inverse scattering problem functions  $G_\gamma$

$$\begin{aligned} G_\gamma(k, \mathbf{R}) &= \sum_l \frac{e^{i\mathbf{l}\mathbf{R}}}{\epsilon_k - \epsilon_l - i\Theta(\mathbf{l} - \mathbf{k}, \gamma)0} \\ &= G^+(\epsilon_k, \mathbf{R}) + \frac{2\pi i}{(2\pi)^3} \int e^{i\mathbf{l}\mathbf{R}} \delta(\epsilon_l - \epsilon) \Theta(\mathbf{l} - \mathbf{k}, \gamma) d^3l d\epsilon \end{aligned} \quad (19)$$

are introduced [13], which asymptotically behave properly in the cone  $|\cos \Theta| \geq (\gamma \frac{k}{k})$  around  $\gamma$ . As it is shown in [13], these functions possess the desired triangle or 'volterra' property so that the solutions  $\Psi_{\gamma k}(\mathbf{r})$  defined with such a kernel, could be represented as having a triangular Fourier transform [13]. With these functions the  $S$ -matrix can be decomposed into a product of two matrices  $Q S = Q^+ Q$  analogously to its decomposition into a product of Jost functions.

If the averaged potential  $V_i$  vanishes at infinity, we can use the result of [13]:

$$\Omega_e = \frac{1}{2\pi} \text{Im} \int_{-\infty}^{+\infty} \text{Sp}(\ln(H - \varepsilon - i0)) d\varepsilon$$

$$= \left\langle \frac{1}{\pi} \int_{-\infty}^{+\infty} \arg \ln \det(H - \varepsilon - i0) d\varepsilon \right\rangle = \left\langle \int h_\gamma(\mathbf{l}, \mathbf{l}) \delta(\varepsilon - \varepsilon_l) d^3l d\varepsilon \right\rangle$$

$$h_\gamma(\mathbf{l}, \mathbf{l}) = \sum_{\mathbf{R}} e^{-i\mathbf{l} \cdot \mathbf{R}} V(\mathbf{R}) u_\gamma(\mathbf{R}, \mathbf{l}) \tag{20}$$

$$u_\gamma(\mathbf{R}, \mathbf{k}) = e^{i\mathbf{k} \cdot \mathbf{R}} + \sum_{\mathbf{R}'} G_\gamma(\mathbf{k}, \mathbf{R} - \mathbf{R}') V(\mathbf{R}') u_\gamma(\mathbf{R}', \mathbf{k}). \tag{21}$$

It is seen that equation (21) is the version of equation (17) with the kernel which, after the integration over angles has asymptotically the triangular form. The function  $h_\gamma$  is the analog of the mass-shell scattering matrix. It is worth noting that in the one-dimensional case  $G_\gamma$  has strictly the triangular form and  $h_\gamma$  is the Jost function. Thus one would expect (21) to give better results than (17) when the influence of the effective medium is included in the boundary conditions, i.e. in the form of the free term in (21). The TP  $\Omega_e$  looks nearly additive relatively to potentials in lattice sites. So the virial decomposition of  $\Omega_e$  into  $n$ -site clusters seems most natural. The interaction with the potentials in cluster sites is considered exactly and the influence of the surrounding medium is taken into account through multiplying the free term in (21) by the trial function  $W(\mathbf{k})$ :

$$u_\gamma(\mathbf{R}, \mathbf{k}) = W(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{R}} + \sum_{\mathbf{R}'} G_\gamma(\mathbf{R} - \mathbf{R}') V(\mathbf{R}') u_\gamma(\mathbf{R}', \mathbf{k}) \tag{22}$$

where the  $W(\mathbf{k})$  value should be found from the  $\Omega_e$  minimization. For the two-site cluster let us rewrite (20) in the form

$$\Omega_e = - \int_{-\infty}^{+\infty} \delta(\varepsilon - \varepsilon_l) \left\{ \langle h^1(\mathbf{l}, \mathbf{l}) \rangle W(\mathbf{l}) \right.$$

$$\left. + \frac{1}{2} \sum_{\mathbf{R} \neq \mathbf{0}} [ \langle h_\gamma^2(\mathbf{l}, \mathbf{l}) \rangle W_\gamma(\mathbf{l}) - 2 \langle h^1(\mathbf{l}, \mathbf{l}) \rangle W(\mathbf{l}) ] \right\} d^3l d\varepsilon \tag{23}$$

where

$$\gamma = \mathbf{R}/R \quad h^1(\mathbf{l}, \mathbf{k}) = V(\mathbf{R}_i) \tilde{u}_\gamma(\mathbf{R}_i, \mathbf{k}) \quad W(\mathbf{k}) = \exp[i\Upsilon(\mathbf{k})]$$

$$h_\gamma^2(\mathbf{l}, \mathbf{k}) = \sum_{m=i,j} e^{-i\mathbf{l} \cdot \mathbf{R}_m} V(\mathbf{R}_m) \tilde{u}_\gamma(\mathbf{R}_m, \mathbf{k}) \quad W_\gamma(\mathbf{k}) = \exp[i(\Upsilon(\mathbf{k}) - \Upsilon_\gamma(\mathbf{k}))] \tag{24}$$

$$\Upsilon(\mathbf{k}) = \sum_{\gamma} \Upsilon_\gamma(\mathbf{k}) \quad \tilde{u}_\gamma(\mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} + \sum_{\mathbf{R}'} G_\gamma(\mathbf{R} - \mathbf{R}') V(\mathbf{R}') \tilde{u}_\gamma(\mathbf{R}', \mathbf{k}).$$

The variation of the equation (23) in  $\Upsilon_\gamma$  gives the equation for determining  $W_\gamma(k)$ :

$$\sum_{\mathbf{k}} [h^2(\mathbf{k}, \mathbf{k})W_\gamma(\mathbf{k}) - h^1(\mathbf{k}, \mathbf{k})W(\mathbf{k})] = 0. \quad (25)$$

With all the  $\Upsilon_\gamma$  being zero, we again restore the average  $t$ -matrix approximation from (23). Calculations with the variational parameters in the  $\Upsilon$  form should take less effort than those in section 2 as the Green function (19) is not changed under iteration. It is worth mentioning that the Schrödinger equation solution with the desired volterra properties can also be obtained on the basis of the regular solution  $\phi_R$  [18], but the equations arising under minimization  $\Omega_c$  in this case have the form of the non-local in the energy equation, which can be reduced to the Hilbert-Riman problem. Furthermore, they depend on the contour choice and are inconvenient for calculations.

#### 4. Calculations of the $\text{Ni}_{1-c}\text{Cu}_c$ alloy density of states by the CFM

In practice in the process of the self-consistent calculations in alloys the electron density  $\rho(r)$  at various atoms should be calculated. Thus the approach developed in section 2 has certain advantages in comparison with that in section 3 as it directly deals with the Green function and thus with the electron density. For this reason the CFM was chosen to calculate density of states in the  $\text{Ni}_{1-c}\text{Cu}_c$  alloys. It follows from the result in [2] that the self-consistent potentials of both components vary slightly with the concentration and thus can be chosen as those in pure metals. It simplifies the calculations significantly especially if the LMTO-ASA method is used. As was shown in [15] in this method the alloy eigenvalue problem is equivalent to the tight-binding (TB) form Hamiltonian with both diagonal and non-diagonal disorder. The results of the TB form of the LMTO-ASA-CPA calculations [19] show that the TB constants corresponding to the bandwidth can be substituted with their mean values

$$\bar{\Delta} = c_a \Delta_a + c_b \Delta_b \quad \bar{\gamma} = c_a \gamma_a + c_b \gamma_b. \quad (26)$$

The designations are as those in [20]. After such approximations the problem is the same as that considered in sections 2 and 3 with the Hamiltonian

$$H_i = C_i + \bar{\Delta}^{\frac{1}{2}} S (1 - \bar{\gamma} S)^{-1} \bar{\Delta}^{\frac{1}{2}} \quad (27)$$

$S(\mathbf{k})$  is the structural matrix. Parameters  $\Delta_i, \gamma_i, C_i$  were self-consistently calculated in pure metals, and their values are summarized in table 1. The Green function  $\tilde{G}_R(z)$  was calculated for every  $z$  and self-energy  $\Sigma(z)$  which altered in the process of iteration. Integration in the Brillouin zone was made by the tetrahedron method with the quadratic interpolation of complex eigenvalues and complex eigenvectors between 102 points in 1/48 of the zone.

Table 1.

	Cu			Ni		
	$C$	$\gamma$	$\Delta^{1/2}$	$C$	$\gamma$	$\Delta^{1/2}$
s	-0.1988	0.4219	0.2881	-0.1580	0.4262	0.3045
p	0.2908	0.1116	0.2707	0.3591	0.1134	0.2842
d	-0.1425	-0.0022	0.0667	-0.0896	-0.0023	0.0771

To check the technique the  $g(\varepsilon)$  CPA calculations were performed. In figure 2 the results are compared with that of the self-consistent KKR-CPA method [2]. We believe that the accuracy of our calculations for this alloy can be assumed as adequate, though in general the problem is not quite clear. In figure 3 we compare the CPA density of states with that obtained in the averaged crystal [1] approximation and with the averaged one-site  $T$ -matrix approach [1]. It is seen that the presence of the effective medium in CPA is very significant and the scattering processes at various sites are not independent (solid and broken curves). In figure 4 the two-site approximation (9), (10), (11a) and the CPA one-site approximation are shown. All the pairs of atoms in the first and second spheres were taken into account. The addition of the second sphere changes the result slightly. (At  $c = 0.23$  and  $\varepsilon = -0.2$ ,  $g(\varepsilon)$  changes from 46.0 to 47.2). Equations (10), (11a) were solved by the Newton method using standard subroutines. It turns out that the corrections to CPA in the present alloy are small. Similar results were obtained for the non-self-consistent cluster calculations in AgPd alloys [21]. Nevertheless there exists a certain decrease of  $g(\varepsilon)$  in the region where the Cu sub-level splits from the d-band and within this interval the  $g(\varepsilon)$  curve is closer to the experiment [2].

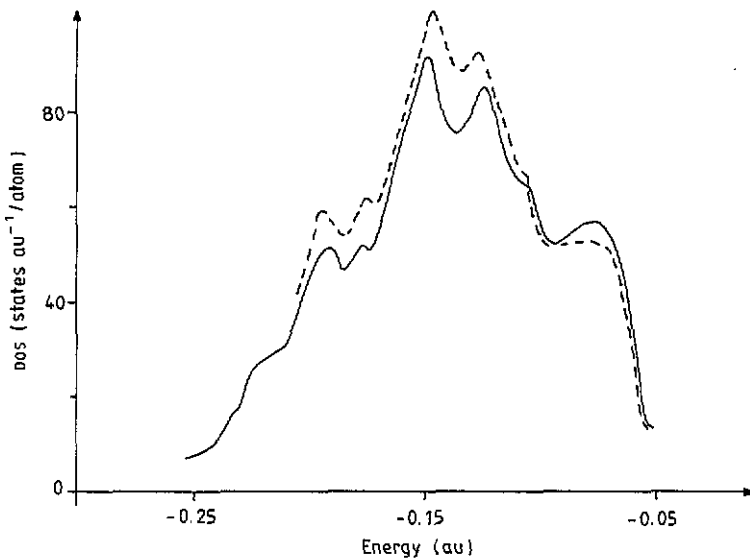


Figure 2. Density of states in the  $Ni_{1-c}Cu_c$  alloy for  $c = 0.23$  by LMT0-ASA-CPA—full curve (present work) and by KKR-CPA [2]—broken curve.

## 5. Conclusion

In the present work the cluster generalization of the CPA method on the basis of the variational approach is suggested. Some alternatives of including the variational parameters in the TP  $\Omega$  virial expansion are proposed. The first of them corresponds to the CVM [4] or its simplified modification CFM [5] used in the theory of ordering alloys. The second approach is closer to the transfer matrix method and can be considered as

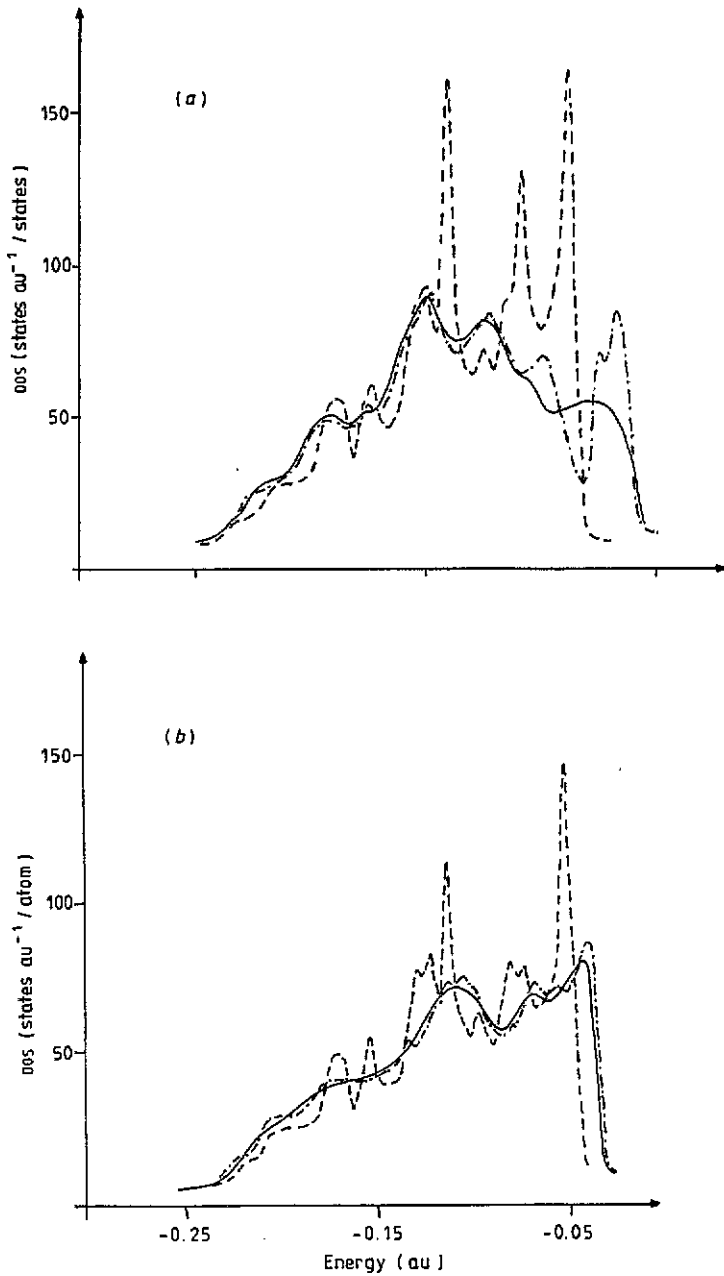


Figure 3. Density of states in the  $\text{Ni}_{1-c}\text{Cu}_c$  alloy calculated by CPA (—), with the mean potential (- - -) and with the mean  $t$ -matrix (- · -). (a)  $c = 0.23$ ; (b)  $c = 0.81$ .

a modification of the embedded method often used in the applied mathematics. The calculations with the cluster containing several sites permit us firstly to evaluate the accuracy of the CPA method and secondly to investigate the question of the influence of the short-range order in the atom distribution over lattice sites on the alloy electronic structure [10], as the probability of finding atoms a and b at two neighbouring lattice

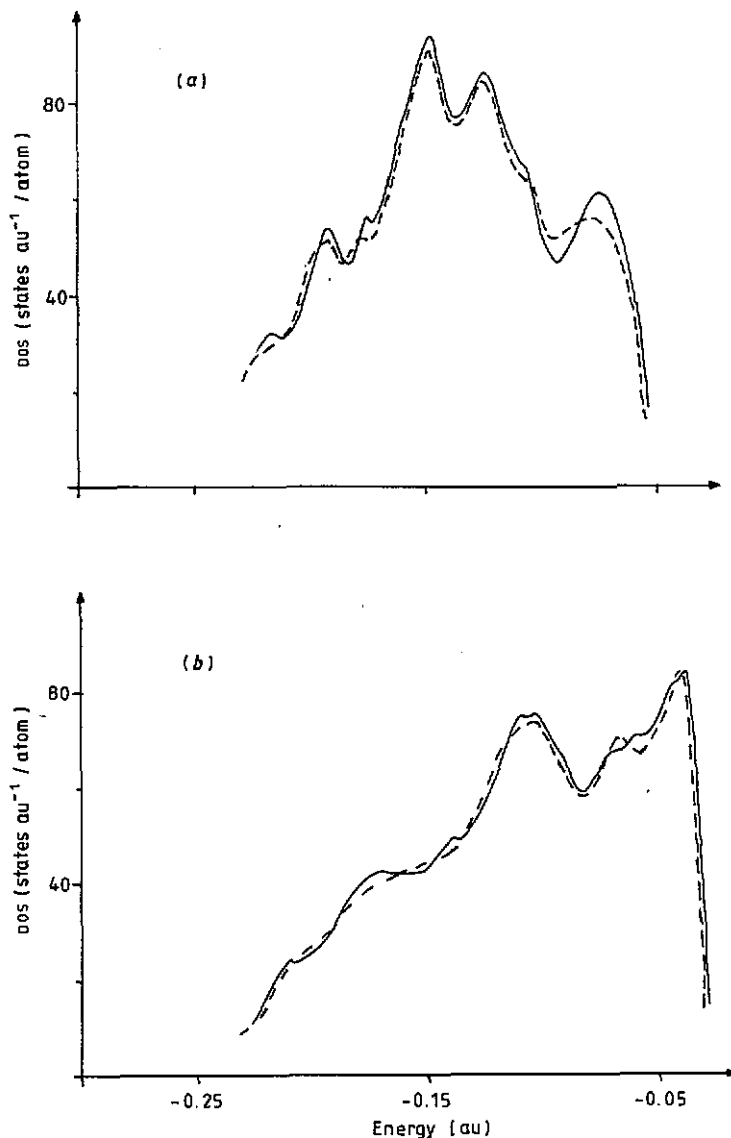


Figure 4. Density of states in the  $\text{Ni}_{1-c}\text{Cu}_c$  alloy calculated with the two-site cluster (—) and CPA (---). (a)  $c = 0.23$ ; (b)  $c = 0.81$ .

sites can be determined from experiment or CVM calculations and can significantly differ from  $c(1-c)$ .

Let us discuss the perspectives of the applications of the present method and its convergence. The CPA method expansion parameter is the value  $\zeta \approx c_a c_b \Delta t / n \sqrt{\epsilon(\epsilon - \epsilon_c)}$  [1] which arises from estimating the non-diagonal in  $R$  terms in the series expansion of the full Green function. Analogous evaluation in the cluster case gives the same expression with the  $\Delta t$  replaced by  $\Delta t_{ab}$ —the difference in scattering properties of the  $a, b$  pair in comparison with those of  $a, a$  and  $b, b$ . Generally speaking this difference is not the simple sum of  $\Delta t_a$  and  $\Delta t_b$ . The situation is similar

to that in the Ising model with the competing  $V_1$  and  $V_2$  interactions. The Bethe approximation truly evaluates contributions of the order  $\Delta \approx V_1 - V_2 \ll V_1$  while the usual molecular field gives corrections of the order of  $V_1/n$ . At the same time both methods are the mean field ones and are inapplicable near the critical points  $\varepsilon_c$ . In our case both methods are inapplicable near singularities of the spectra where  $g(\varepsilon)$  is, for example,  $\approx \sqrt{(\varepsilon - \varepsilon_c)}$ , but in cases when the multiple scattering in two atoms strongly differs from that on the single atom, the application of the cluster method may be necessary. Such an example exists in the one-dimensional case [22].

But the main differences between the CPA and the cluster approach appear to be revealed in the calculations of configurational interactions  $V_{ij}$ , when the  $n$ -site cluster is embedded in the effective medium. Firstly the  $V_{ij}$  values are the 'differential' values which are more sensitive to the basis of the calculations and secondly it is important that the effective medium should be in agreement with the cluster to gain the self-consistency of the charge fluctuations.

In the present work the cluster approximation has been discussed for the tight-binding Hamiltonian model (though hopping on distant sites and thus the arbitrary dependence of the electron bands on  $k$  were permitted) and diagonal disorder. The inclusion of non-diagonal disorder demands either additional variational parameters or the technique of using the LMTO potential function  $P(\varepsilon)$  or even using the power of the full KKR method. Generalizations of all the expressions on these cases are quite obvious.

Authors are indebted to V G Vaks for numerous discussions and for pointing out the inaccuracies in the initial version of this paper, and to A V Fedorov for the critical reading of the manuscript.

## Appendix

The problem of calculating energies  $E_n$  of certain configurations of 'impurities'  $a, b, \dots$ , distributed in sites  $i_1, i_2, \dots, i_n$ , with the averaging over all the other sites arises in the process of the  $n$ -site configurational interactions calculations. Example diagrams corresponding to such calculations are shown in figure 5(a). The simplest vertex  $\Gamma(R_a, R, R)$  is shown in figure 5(b). The physical interpretation of these results is that it is possible for electrons to scatter on nearest random ions under the condition that a certain potential is fixed in the a point.

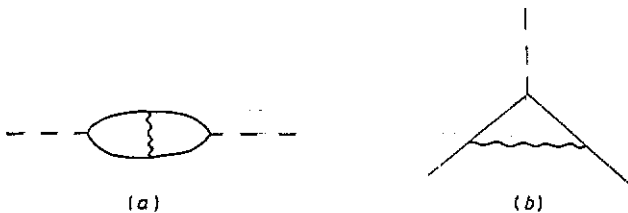


Figure 5. (a) A typical diagram for the configurational interaction  $V_{ij}$ ; (b) The simplest vertex.

The possibility of the application of the variational approach to the calculation of the vertex function  $\gamma(R) = \Gamma(R_a, R, R) - 1$  will be illustrated below with the example of the 2-site cluster. Let us add the potential  $V_a \gamma_a$  in the one-site cluster and

$V_a(\gamma_a - \gamma_{a\rho})$  in the two-site cluster with the sites  $R_a$  and  $R_b = R_a + \rho$  so that after the summation over all sites and clusters we obtain zero:

$$\gamma_a(\mathbf{R}) = \sum_{\rho} \gamma_{a\rho}(\mathbf{R}). \quad (\text{A1})$$

Then

$$\begin{aligned} \Omega = \Omega_0 + \langle \ln[1 - V_a(1 + \gamma_a)G] \rangle + \frac{1}{2} \sum_{\rho} \{ \langle \ln[1 - V_a(1 + \gamma_a - \gamma_{a\rho})G] \\ - V_b(1 + \gamma_b - \gamma_{b-\rho})G \rangle - \langle \ln[1 - V_a(1 + \gamma_a)G] \rangle \\ - \langle \ln[1 - V_b(1 + \gamma_b)G] \rangle \}. \end{aligned} \quad (\text{A2})$$

The variation of equation (A2) over  $\gamma_{a\rho}$  with the additional condition (A1) gives equations for finding  $\gamma_{a\rho}$ . As  $\gamma_a(\mathbf{R})$  takes into account the correlation in two sites  $a$ ,  $R$ , the system of equations obtained is much more cumbersome than (10). Of course its numerical solution needs further investigation. But it seems to us that the possibility itself of finding  $\gamma_a$  illustrates the flexibility of the variational approach using  $\Omega$  minimization.

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