

Determination of effective-pair interactions in random alloys by configurational averaging

H. Dreyssé

*Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
and Laboratoire de Physique du Solide, Université de Haute Alsace, 68093 Mulhouse CEDEX, France*

A. Berera

*Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
and Department of Physics, University of California, Berkeley, California 94720*

L. T. Wille

Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

D. de Fontaine

*Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
and Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720*

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A real-space method is presented for calculating effective-pair interactions (EPI's) in substitutionally disordered alloys, starting from electronic structure information for the constituting elements. The EPI's are obtained by averaging over a small number of randomly generated configurations. The electronic structure is calculated by tridiagonalizing a tight-binding Hamiltonian using the recursion method. Convergence, both as a function of the number of configurations and the number of recursion levels, is rapid, and the results compare very well with other calculations. The advantage of the present scheme is that deviations from lattice periodicity can be taken into account in a completely straightforward way. The EPI are essential ingredients in statistical methods for determining alloy phase diagrams.

I. INTRODUCTION

The electronic structure is the driving force behind a large variety of physical and chemical properties of solids.¹ The phase formation and stability of substitutionally disordered solid solutions are examples of such properties and it is their determination which is the object of the present work.² The most successful statistical models depend on the availability of reliable approximate expressions for the configurational energy and entropy. These are most conveniently formulated in terms of effective-pair (and, if necessary, larger cluster) interactions. Such interactions can, in principle, be measured experimentally through diffuse intensities in neutron and x-ray scattering³ for example. Several phenomenological approaches have been proposed in the past as well.⁴ However, in keeping with a general trend in recent years, the possibility of a first-principles calculation of effective-pair interactions (EPI) has received increasing attention by various groups. Several schemes have been developed and investigated. One possibility is to start from density-functional total-energy calculations for the perfectly ordered compounds.^{5,6} Alternatively, one can perturb the completely disordered alloy in several ways: by imposing a concentration wave,⁷ by means of the generalized perturbation method,⁸ or using embedded clusters.^{9,10} All of these methods have closely related free-energy expansions.¹¹ The electronic structure of the disordered compound is mostly frequently determined

within the coherent-potential approximation (CPA).¹² The CPA is a mean-field theory for the completely random alloy and has been shown to be optimal within the single-site approximation. It has been applied very successfully to a wide variety of disordered metallic alloys. However, attempts to go beyond the single-site approximation suffer from severe analyticity problems. Thus, the inclusion of short- or long-range order in the CPA framework is by no means straightforward.

In the CPA an effective medium is constructed through a self-consistency requirement on the scattering operators and the electronic properties are calculated, either by tight-binding or multiple scattering [Korringa-Kohn-Rostoker (KKR)] techniques. More generally, any alloy electronic structure calculation involves these two steps: "averaging" and band structure determination. In the present work, it is proposed to interchange these steps. That is, one first determines the electronic structure for a randomly generated configuration (the only constraint being a fixed concentration) and the resulting physical quantities are averaged over a sufficiently large number of independent configurations. This procedure can be implemented very efficiently using the recursion method¹³ applied to a tight-binding Hamiltonian as will be discussed herein. Certainly, the idea of configurational averaging is not new¹⁴ and everything depends on the rate of convergence with respect to the number of configurations needed. Earlier work focused mostly on densities of states (DOS), for which it was concluded that

it was necessary to perform an exact average over the first shell of neighbors in the fcc lattice.¹⁵ Since this involved 144 inequivalent configurations, the method was very time consuming and has not been widely used, although the agreement with the CPA was satisfactory as well as the extension to partially ordered systems.¹⁶ Moreover, for the bcc lattice the scheme could become intractable, since it is very likely that exact averages would need to be performed over the first and second shell, because the bcc structure does not contain any triangles entirely confined to nearest neighbors in the first shell.

It will be shown in this work that it is not necessary to enumerate all possible occupancies of the first shell to obtain accurate EPI, but that a rather small number of configurations, say ten, is sufficient. The reason for this faster convergence, compared to DOS, is that the EPI are essentially integrated quantities, i.e., total-energy differences of different pairs in the alloy, and therefore they are less sensitive to local perturbations that conserve the total number of electrons. An attractive feature of the recursion method is that it is not necessary to calculate individual cohesive energies for the different pairs, which would lead to a large subtractive cancellation of terms. Rather, it is possible to compute these quantities directly in the recursion formalism and in this way avoid numerical instabilities.

The feasibility of this new approach has already been illustrated in a previous short paper¹⁷ for canonical tight-binding parameters and d bands only. In the present work the underlying formalism is worked out in more detail and the treatment is extended to include s and p orbitals. In a first group of calculations arbitrary, but realistic, tight-binding parameters were selected for an alloy A_cB_{1-c} in which the number of d electrons N_A (N_B) was equal to 3 (8). In a second group of calculations first-principles parameters appropriate for the binary system $\text{Rh}_c\text{Ti}_{1-c}$ were used. The remainder of this paper is organized as follows. Section II sets out the background and theoretical aspects of the present approach and discusses some numerical details. Section III is devoted to a discussion of the results for the "3-8" system and the binary alloy $\text{Rh}_c\text{Ti}_{1-c}$. EPI obtained by the present method are presented and the convergence as a function of the number of levels and the number of configurations is analyzed. As a first step towards a phase-diagram calculation, heats of mixing for the different phases in $\text{Rh}_c\text{Ti}_{1-c}$ are computed. The paper concludes with a summary and some comments in Sec. IV.

II. FORMALISM

A given configuration σ of the binary system can be described by the following tight-binding Hamiltonian:

$$H(\sigma) = \sum_{n,\lambda} |n,\lambda\rangle \epsilon_n^\lambda \langle n,\lambda| + \sum_{\substack{n,m \\ n \neq m, \lambda, \mu}} |n,\lambda\rangle \beta_{nm}^{\lambda\mu} \langle m,\mu|, \quad (2.1)$$

where n and m are lattice sites and λ and μ label the orbitals ($\lambda, \mu = 1, \dots, 9$ for s, p , and d orbitals). The on-site

energies ϵ_n^λ depend, strictly speaking, on the local environment in the disordered system, but one often makes the approximation to replace them by elemental values ϵ_n^A or ϵ_n^B depending on whether site n is occupied by an A or a B atom (diagonal disorder). It will be seen, however, that such a simplification would lead to unphysical results in the present case. The hopping parameters $\beta_{nm}^{\lambda\mu}$ are likewise restricted to three values β^{AA} , β^{BB} , or β^{AB} . In the Slater-Koster¹⁸ parametrization scheme, these are related to the three- and two-center integrals for the pure elements. Off-diagonal disorder is usually taken into account by geometrically averaging the pure element hopping parameters¹⁹

$$\beta^{AB} = (\beta^{AA}\beta^{BB})^{1/2}. \quad (2.2)$$

Several methods are available for obtaining tight-binding parameters for the pure elements. Canonical values (for d bands only) have been used quite successfully to predict ordering tendencies and lead in some cases to remarkable agreement with experiment.^{20,21} A semi-phenomenological set of parameters has been tabulated by Harrison.²² Closer to a first-principles determination are the values obtained by Papaconstantopoulos²³ by a least-squares fit to linear augmented-plane-wave (LAPW) band structures. Potentially the most accurate first-principles results are those given directly by the tight-binding-linear-muffin-tin-orbital (TB-LMTO) method of Andersen and co-workers.²⁴

The recursion method¹³ provides an algorithm for calculating diagonal matrix elements of the resolvent or Green's function, associated with the Hamiltonian (2.1) and defined as

$$G(z) = (z - H)^{-1}. \quad (2.3)$$

Given a starting state $|u_0\rangle$, one generates a discrete chain of vectors, $|u_i\rangle$, which can be constructed to be orthonormal, through the following set of operations:

$$b_0^2 = \langle u_0 | u_0 \rangle, \quad (2.4a)$$

$$a_i = \langle u_i | H | u_i \rangle, \quad (2.4b)$$

$$H | u_i \rangle = a_i | u_i \rangle + b_{i+1} | u_{i+1} \rangle + b_i | u_{i-1} \rangle. \quad (2.4c)$$

This prescription essentially transforms the Hamiltonian into (Hermitian) tridiagonal form and thus leads directly to a continued fraction representation for the Green's function matrix element $\langle u_0 | G | u_0 \rangle$. If the algorithm is stopped after L steps, L exact levels of the continued fraction are obtained. This computational scheme is also closely related to the theory of orthogonal polynomials, a fact that can be exploited in the development of stable and efficient computer codes.²⁵ One of the attractive features of the recursion method is the fact that it allows for a direct physical interpretation, apart from its formal mathematical elegance. Indeed, it is clear from Eqs. (2.4) that the matrix element after L levels contains the exact contributions from all closed paths of L steps starting and ending at the central orbital. Thus if one tries to model an infinitely extended system, the recursion algorithm after L steps contains contributions only from a

central cluster consisting of $O(L^3)$ atoms. For numerical purposes, this limits the number of atoms that can be modeled, and also implies that one is always studying a finite system. In order to reduce the necessary amount of computer storage, it is possible to decouple the number of levels and the number of atoms in the cluster, a point that will be pursued in the next section. In either case, a terminating continued fraction is obtained, which yields a number of isolated bound states, appropriate for a finite cluster. For most purposes this is an unphysical approximation to the problem under investigation and some way needs to be found to eliminate finite-size effects by embedding the cluster in an infinite medium. Mathematically, this means that a terminator must be appended to the continued fraction expansion, so as to obtain a Green's function with a branch cut, rather than a set of simple poles. The problem of finding a terminator that gives an optimal description of the surrounding medium has been studied in many papers (Ref. 26 and references therein) and several prescriptions are available. It has been established in our previous paper¹⁷ that the EPI (for transition-metal alloys) are not very sensitive to the exact nature of the terminator and therefore the simple quadratic terminator can be used with confidence. This amounts to putting all a_i and b_i with $i > L$ equal to a_L and b_L , and approximates the density of states of the embedding medium with a semielliptical band.

Although most applications of the recursion method involve the determination of the (local) density of states, any observable that can be related to the Green's function (2.3) can be calculated recursively.²⁷ In particular, the present work is aimed at the calculation of effective-pair (and cluster) interactions in disordered alloys, quantities that are the main ingredients in statistical techniques such as the cluster-variation and Monte Carlo method. In these treatments, averages are taken involving the density function $\rho(\sigma)$, which gives the probability of finding a specific configuration σ in an ensemble of systems. This function is given by

$$\rho(\sigma) = Z^{-1} e^{-E(\sigma)/kT}, \quad (2.5)$$

where Z is the partition function

$$Z = \text{Tr}^{(N)} e^{-E(\sigma)/kT}, \quad (2.6)$$

and the trace operator $\text{Tr}^{(N)}$ denotes a sum over all configurations of a system with N sites. In the work of Sanchez *et al.*²⁸ it has been shown that the state of order of an alloy can be expressed in terms of a complete set of orthogonal functions involving various clusters, used to approximate the configurational entropy. The function relative to cluster α is defined as

$$\Phi_\alpha(\sigma_\alpha) = \sigma_1 \sigma_2 \cdots \sigma_n, \quad (2.7)$$

where the σ_i are pseudospin variables (+1 if site i is occupied by an A atom, -1 otherwise). Any function of the alloy configurations can be expanded in terms of these functions; in particular, the density function (2.5) can be written as

$$\rho(\sigma) = 2^{-N} \left[1 + \sum_\alpha \Phi_\alpha(\sigma) \xi_\alpha \right], \quad (2.8)$$

where

$$\xi_\alpha = \langle \Phi_\alpha(\sigma) \rangle \quad (2.9)$$

is one of a hierarchy of linearly independent correlation functions. The internal energy of the alloy system can be written as a functional of the density

$$E[\rho] = \text{Tr}^{(N)} \rho(\sigma) E(\sigma), \quad (2.10)$$

or, after substitution of (2.8),

$$E = \varepsilon_0 + \sum_\alpha E_\alpha \xi_\alpha, \quad (2.11)$$

where

$$\varepsilon_0 = 2^{-N} \text{Tr}^{(N)} E(\sigma) \quad (2.12)$$

is configuration independent, and

$$E_\alpha = 2^{-N} \text{Tr}^{(N)} \Phi_\alpha(\sigma) E(\sigma) \quad (2.13)$$

are the effective-cluster interactions. For a pair of atoms, one at site p and one at site q , the trace in (2.13) can be broken up into two parts, one over the points p and q , and one over the remainder of the configuration, which leads to the final expression

$$E_{pq} = \frac{1}{4} (V_{AA} - V_{AB} - V_{BA} - V_{BB}), \quad (2.14)$$

where V_{IJ} is the total energy of a pair I (at site p), J (at site q) embedded in the average medium at a given concentration, or explicitly²

$$V_{IJ} = 2^{2-N} \text{Tr}^{(N-2)} E(I, J; \sigma'), \quad (2.15)$$

where $E(I, J; \sigma')$ is the energy of a configuration σ consisting of atom I (J) at site p (q), with the remaining sites denoted by σ' . It is seen that the V_{IJ} are total energies and, as such, cannot be obtained from a pair-potential model.⁸ But ordering energies result from taking differences of large terms and are known to converge satisfactorily taking only effective-pair interactions.⁸ In a similar fashion one can define triplet and higher-order interactions, for example,

$$E_{pqr} = \frac{1}{8} (V_{AAA} - 3V_{AAB} + 3V_{ABB} - V_{BBB}), \quad (2.16)$$

in an obvious notation and assuming that all sites are equivalent. Typically, these ordering energies converge quickly as a function of cluster size and interatomic distance, but the expressions (2.14) and (2.16) are not very useful for computer calculations, since one needs the difference of nearly equal large numbers. However, it turns out that the "orbital peeling trick" developed by Burke,²⁹ following the work of Einstein and Schrieffer,³⁰ permits a direct calculation of the EPI, as will now be shown.

In the Hartree-Fock approximation, the total energy of a solid consists of two terms, a one-electron band-structure contribution V_{BS} and an electrostatic term V_{ES} , which includes the double counting correction and the ionic repulsion. It is usually assumed that upon taking differences like in (2.14), the electrostatic contributions cancel out and one is left with solely the one-electron band-structure term.³¹ Thus, what is needed to calculate

the EPI is an average over all configurations σ , with fixed occupancy of sites p and q , of the one-electron band-structure term

$$V(\sigma) = \int_{-\infty}^{E_F} E n(E, \sigma) dE, \quad (2.17)$$

where $n(E, \sigma)$ is the electronic DOS and E_F is the Fermi level, independent of the configuration σ .

At this point it is important to specify the choice of the basis set. Often in substitutional impurity problems one assumes a unique set of orbitals at each site and thus the impurity is described using the same orbitals as the atom that was removed (Ref. 32 and references therein). This may be a bad approximation, in particular if the two atomic species that are involved are very dissimilar. However, the adspace-subspace description developed by Williams *et al.*³³ and extended by Riedinger³⁴ avoids this shortcoming and provides a more general setting for this type of studies. In an EPI calculation two atoms need to be embedded and therefore a basis set Ω is defined as follows:

$$\Omega = \omega \cup A_p \cup A_q \cup B_p \cup B_q, \quad (2.18)$$

where ω is the set of atomic orbitals describing the host (the recursion cluster except for the sites p and q), A_p and A_q (B_p, B_q) are sets of atomic orbitals for an A (B) atom at site p , respectively, q . In this formalism the Hamiltonian for an A atom at site p and a B atom at site q , for example, would be written in block form as

$$H_{AB} = \begin{pmatrix} H_A^p & 0 & 0 & H_{AB} & H_{AO} \\ 0 & H_A^q & 0 & 0 & 0 \\ 0 & 0 & H_B^q & 0 & 0 \\ H_{BA} & 0 & 0 & H_B^p & H_{BO} \\ H_{OA} & 0 & 0 & H_{OB} & H_O \end{pmatrix}, \quad (2.19)$$

where H_A^{∞} and H_B^{∞} are the Hamiltonians for the isolated atoms, H_A^p (H_B^q) are the Hamiltonians describing the A (B) atom at site p (q), H_O is the Hamiltonian for the host and the other matrices couple the different subsystems. This representation is overcomplete, but this introduces no errors, since only one set of orbitals for each site is coupled to the host in each of the four cases needed in (2.14). The adspace-subspace description also eliminates the potential problems due to particle nonconservation; two atoms, namely those that are not coupled to the rest of the system, can be thought of as located at infinity. The physical system then consists of these two isolated atoms and the full recursion cluster. Thus the total number of atoms of each species is the same in all four cases in (2.14).

The process involved in an EPI calculation is the interchange of two atoms. The self-consistency procedure, which takes into account the charge transfer, consists of a shift of the diagonal elements of the Hamiltonian³⁵

$$\epsilon_n^{\lambda} = \epsilon_n^{\lambda,0} + \sum_{\mu} U_n^{\mu} N_n^{\mu} + \sum_m V_{nm}^{\lambda} N_m^{\lambda}, \quad (2.20)$$

where $\epsilon_n^{\lambda,0}$ is the atomic energy level, N_n^{λ} is the total

charge corresponding to orbital λ at site n , and $U_n^{\lambda}, V_{nm}^{\lambda}$ are the intra- and inter-atomic Coulomb integrals. In the case of a disordered alloy studied here, one would *a priori* need to determine ϵ_n^{λ} for each atom. This is clearly an impossible task. The crudest approximation is to consider only two different atomic levels ϵ^A and ϵ^B , independent of the atomic environment. As a first improvement on this scheme, one can allow for changes in the potential (ϵ_n^{λ}) only for the atoms at the sites p and q . In these two cases H_O does not depend on the nature of the atoms at positions p and q . A further refinement of this approach would be to include some potential perturbations on the atomic sites surrounding the atoms at p and q . In fact, as will be seen in the next section, it turns out that taking ϵ_n^{λ} independent of the position n yields good results for the EPI, but is insufficient for the mixing energies. In the following, it will be assumed that the host Hamiltonian H_O is independent of the nature of the atoms at sites p and q .

The electronic DOS is related to the Green's function through the equality

$$n_{IJ}(E) = -\frac{1}{\pi} \text{Im Tr } \mathcal{G}_{IJ} \equiv -\frac{1}{\pi} \text{Im Tr } (E - \mathcal{H}_{IJ})^{-1}, \quad (2.21)$$

where $\mathcal{H}_{IJ}$ is the Hamiltonian for the full system, of the form (2.19). It is well known that this can be written as

$$n_{IJ}(E) = \frac{1}{\pi} \text{Im } \frac{\partial}{\partial E} \ln \det(E - \mathcal{H}_{IJ}), \quad (2.22)$$

which will be the starting point for the numerical calculations. It is now obvious that the EPI can be written as

$$E_{pq} = \frac{1}{4} \int_{-\infty}^{E_F} dz z \text{Im } \frac{d}{dz} \eta(z), \quad (2.23)$$

where $\eta(z)$ is the generalized phase shift given by

$$\eta(z) = \ln \frac{\det \mathcal{G}_{AA} \det \mathcal{G}_{BB}}{\det \mathcal{G}_{AB} \det \mathcal{G}_{BA}}. \quad (2.24)$$

The Friedel sum rule, which expresses the conservation of the total number of electrons, can be written quite generally as

$$\int_{-\infty}^{E_F} dz \text{Im } \frac{d}{dz} \eta(z) = 0. \quad (2.25)$$

Now, integrating by parts in (2.23) and using the Friedel rule, one finally finds for the EPI

$$E_{pq} = -\frac{1}{4\pi} \text{Im } \int_{-\infty}^{E_F} \eta(z) dz. \quad (2.26)$$

It is obviously out of the question to calculate the full determinants in Eq. (2.22), since they are of the order $N \times v$, where N is the number of atoms in the cluster and v the number of orbitals per site. Since in the exchange of the atoms on sites p and q the perturbation is of finite range, the phase shift $\eta(z)$ has a finite size, as can also be seen as follows. From the properties of a partitioned matrix it follows that:²⁹

$$\det(E - \mathcal{H}_{IJ}) = \det G_{IJ}^{-1} \det(E - H_O), \quad (2.27)$$

$$\eta(z) = \ln \frac{\det G_{AA} \det G_{BB}}{\det G_{AB} \det G_{BA}}. \quad (2.28)$$

Thus, it is not necessary to calculate the determinant of order $(N-4)\nu \det(E - H_O)$, which otherwise would lead to an unacceptable increase in computer time.

All that remains is the calculation of the generalized phase shift (2.24), and this can be done efficiently by means of the "orbital peeling" scheme as will now be discussed. For short, denote by $\mathcal{A}$ any one of the four matrices $(E - \mathcal{H}_{IJ})$

$$\mathcal{A} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1,M-1} & a_{1M} \\ a_{21} & a_{22} & \cdots & a_{2,M-1} & a_{2M} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ a_{M-1,1} & a_{M-1,2} & \cdots & a_{M-1,M-1} & a_{M-1,M} \\ a_{M1} & a_{M2} & \cdots & a_{M,M-1} & a_{MM} \end{bmatrix} \begin{matrix} A_1 \\ A_2 \\ \vdots \\ A_{M-1} \\ A_M \end{matrix} \quad (2.29)$$

with $M = N\nu$ and "principal" submatrices $A_1, \dots, A_M$ have been indicated. For any $1 \leq k \leq M$ one has, with $D_k = \det A_k$

$$\frac{D_{k+1}}{D_k} = \bar{g}_k, \quad (2.30)$$

where $\bar{g}_k$ is the top left element of the inverse of A_k . From this it follows that

$$\begin{aligned} & G[(A-A)/1] + G[(V-A)/2] + G[(B-B)/1] + G[(V-B)/2] \\ & - G[(A-B)/1] - G[(V-B)/2] - G[(B-A)/1] - G[(V-A)/2] \\ & = G[(A-A)/1] + G[(B-B)/1] - G[(B-A)/1] - G[(A-B)/1]. \end{aligned} \quad (2.33)$$

Thus this quantity is computed by "peeling" only on the atom at position 1 for each of the four possible configurations.

The choice of the Fermi level and the description of the Hamiltonian used pose delicate questions in the case of a disordered alloy. One cannot simply assume that the on-site energies depend only on the nature of the atoms in the disordered alloy and use the tight-binding parameters for the pure elements (ϵ_A^s , ϵ_A^p , ϵ_A^{t2g} , and ϵ_A^e , and likewise for the B atoms), since coupling A and B will introduce changes in these energies. In the present work a rigid shift δ of the pure compound values for one species, say B , will be assumed. That is, the values of the on-site energies for the A atoms will be left unchanged from those of the pure element, while the B values are taken to be $\epsilon_B^s + \delta$, $\epsilon_B^p + \delta$, $\epsilon_B^{t2g} + \delta$ and $\epsilon_B^e + \delta$. Thus, for a given concentration one has to determine this parameter δ as well

$$\prod_{k=1}^M \bar{g}_k = \frac{1}{\det \mathcal{A}}. \quad (2.31)$$

Using these representations in (2.28) and keeping in mind that common factors cancel, one finds

$$\eta(z) = \sum_{k=1}^{4\nu} \ln \frac{\bar{g}_k^{AA} \bar{g}_k^{BB}}{\bar{g}_k^{AB} \bar{g}_k^{BA}}. \quad (2.32)$$

Each $\bar{g}_k^{IJ}$ is the top left element of a partial Green's matrix, with the designated atom at sites p and q . It can be seen that only diagonal elements of the Green's function are needed, but that each $\bar{g}_k^{IJ}$ must be calculated separately for each of the 4ν cases: The 4ν orbitals are "peeled off" one by one²⁹ and this can be readily included in the recursion framework.²⁵ In this method matrix elements $\bar{g}_k$ are obtained, with every row and column of the Hamiltonian with an index $i < k$ equal to zero.

It is important to note that only four atoms need to be "peeled." Obviously a cancellation of terms occurs from the matrices H_A^∞ and H_B^∞ since these are diagonal and not coupled to the system. Thus for each pair (I, J) , one has two atoms to peel, but it is possible to show that because of the symmetry in the definition of the EPI, for each pair (I, J) only one atom needs to be "peeled." To this end one defines $G[(X-Y)/i]$ as the term obtained by "peeling" for a pair $X-Y$ the orbitals for the X atom on site i where X and Y are A , B or a vacancy, denoted by V and $i = 1, 2$ referring to site p and q , respectively. The term $\det G_{AA} \det G_{BB} / \det G_{AB} \det G_{BA}$ in the phase shift can then be written symbolically as

as the Fermi level E_F . Since a fully self-consistent calculation is not feasible for the disordered case, as discussed previously, these values have been calculated for the pure elements as well as the ordered structures (AB , A_3B , and AB_3) under the assumption of local charge neutrality. If, for a given structure, two or more atoms of a given type are present (like the two inequivalent B sites in the DO_3 structure with composition AB_3), an average is made. For other concentrations (in the disordered state) δ and E_F are found by interpolating between the values for the pure compounds. In general, a linear variation of E_F and δ with concentration is obtained, comparable with a Taylor's expansion truncated after the second term.

For the calculation of EPI this scheme gives satisfactory results. Mixing energies, however, are differences of integrated quantities and it turns out that this approach needs to be refined. The mixing energy for the complete-

ly disordered state, for example, is given by

$$\Delta E_m^{\text{dis}(c)} = c \left\langle \int_{-\infty}^{E_F} E n^A(E) dE \right\rangle + (1-c) \left\langle \int_{-\infty}^{E_F} E n^B(E) dE \right\rangle - (1-c)E_A - cE_B, \quad (2.34)$$

where E_A and E_B are the cohesive energies of the pure elements. The first two terms in this expression are computed by means of configurational averaging in a manner completely similar to the EPI. That is, the one-electron band-structure term is calculated, with a given site first occupied by an A atom and then by a B atom. It turns out that a simple rigid shift of the on-site energies gives insufficient accuracy as far as mixing energies are concerned. A first improvement is to allow for a shift of the Fermi level on the central atom, so as to satisfy some property, for example, since charge transfer is small in metallic systems, one can impose local neutrality. This approach can be understood by the following argument: The small shift of the Fermi level arises because of the replacement of an atom.³⁰ In such a case no perturbing potential exists to screen the electronic charge displaced because of the exchange of atoms. The shift in the Fermi level is small and can be considered within a perturbation framework. To first order it is equivalent to having an unknown perturbing potential on the site under consideration. Rather than introducing such an adjustable parameter, the Fermi-level shift is calculated self-consistently in the present scheme. Finally, it must be pointed out that further improvements can be made by applying the perturbation method developed by Foulkes and Haydock,²⁷ but this is outside the scope of the present work.

III. RESULTS

The formalism described in the previous section has been applied to calculate nearest-neighbor and next-nearest-neighbor EPI's in the fcc and bcc lattice for two types of transition metal alloy systems. In the first group of calculations, in which the configurational averaging method was tested for convergence and other general properties, s , p , and d orbitals were considered for a fictitious 3-8 system. To this end, arbitrary, but realistic, tight-binding parameters were taken to represent a disordered A_cB_{1-c} alloy in which the number of d electrons N_A (N_B) was equal to 3 (8) and giving a d band width of 1, (defining thus the energy unit) and reasonable positions and shape of the s and p bands. As a consequence, all results are expressed in arbitrary units (arb units). This case will be called "3-8". Subsequently, the binary alloy $\text{Rh}_c\text{Ti}_{1-c}$, which is one example of such a system, was investigated using the tight-binding values tabulated by Papaconstantopoulos.²³ Off-diagonal disorder was treated by means of Shiba's prescription (2.2). Note, however, that this is an approximation that need not be made in a real-space method, provided that hopping parameters for the ordered compound AB are known. The

configurational average $\langle \dots \rangle_{IJ}$ was calculated by generating random configurations (at fixed concentration) and averaging the resulting EPI, a procedure that has been shown to converge quickly.¹⁷

In the remainder of this paper, EPI obtained by configurational averaging will be presented and their general properties discussed. A unique δ and E_F , function of the concentration c , will be considered. However, for the purpose of illustration, the EPI will be plotted as a function of the position of the Fermi level. Strictly speaking, since a constant value of δ has been used, the results are only valid at the exact Fermi level for the "3-8" alloy. It seems reasonable though to assume that the general trends in the EPI will be found in this way,³⁶ and this approach also provides a general check on the method.

As noted before, the computing time grows very quickly as a function of the number of levels in the continued fraction. To illustrate this point, Fig. 1 shows results for the nearest-neighbor EPI in the fcc structure with "3-8", values and $c_A=0.25$. It can be seen that the necessary cpu time (plotted in arbitrary units) grows rapidly with increasing number of levels. This rapid growth puts a serious limit on the number of levels for which the recursion scheme is computationally tractable. Next, Fig. 2 shows the same nearest-neighbor EPI as a function of the number of configurations (N) and the number of levels (L). It can be seen that the convergence as a function of N is very fast; the results for $N=10$ and $N=20$ are virtually identical. As a function of L , the asymptotic value seems to be approached quite closely for $L=7$ or 8. These results are similar to those found before¹⁷ and exhibit the same trends. The uncertainty in the EPI after averaging over 10 configurations is approximately 1% and improved accuracy can be obtained by increasing the number of levels, rather than the number of configurations. It is interesting to note that the self-consistency parameters, i.e., the Fermi-level E_F and the

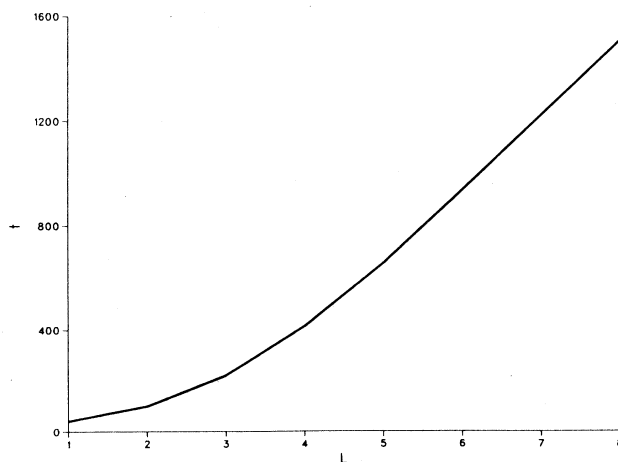


FIG. 1. CPU time (in arbitrary units) for a full EPI calculation as a function of the number of levels (L) in the continued fraction.

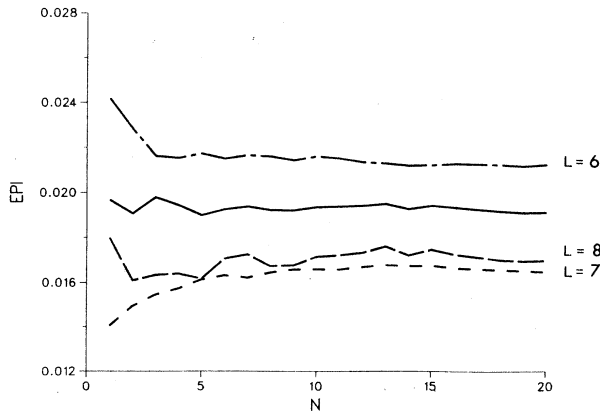


FIG. 2. Nearest-neighbor EPI (in arbitrary units) in the fcc structure for “3-8” values with $c_A=0.25$, as a function of the number of configurations (N) and the number of levels (L). Solid curve: $L=7$, but with self-consistency parameters for $L=8$. In all cases the same set of random configurations was used.

on-site energy shift δ (which are functions of the number of levels), have a considerable influence on the EPI's. The solid curve is obtained by using seven recursion levels, but with the self-consistency parameters corresponding to eight. The resulting EPI (obtained by averaging over identical random configurations in all cases) deviates strongly from that obtained for seven and eight levels, with the appropriate E_F and α_n^λ . Similar calculations were made for a bcc alloy, taking into account interactions up to third neighbors. The results show that for an fcc alloy with first- and second-neighbor interactions, seven levels of the continued fraction are necessary, while for the bcc alloy only six levels are needed. In general, the error is of the order 0.01 eV and depends only weakly on the actual values of the EPI. Thus it appears that the uncertainty in the EPI obtained by configurational averaging is an absolute one. Finally, it also needs to be pointed out that the convergence as a function of the number of levels is faster for a disordered system than for an ordered one (see also Fig. 3).

From the foregoing it can be concluded that increasing the number of levels in the continued fraction expansion leads to improved accuracy, but that this is accompanied by a prohibitive increase in computer time. Therefore it is logical to decouple the number of levels and the number of atoms in the cluster, and it will now be shown how this can be done. To determine the set of coefficients in the continued fraction, one can use the “zebra” developed by Dreyssé and Riedinger.³⁷ This procedure builds a cluster organized into shells in such a way as to guarantee that the resulting structure has the minimal size compatible with the number of levels used. In standard approaches, one would use a more spherical cluster. Using the “zebra” method saves time in that one avoids evaluating the matrix elements to atoms outside the “zebra”, which are all vanishing. In this way no additional sources of error are introduced. It has been conjectured³⁷ that the size of the cluster grows as L^d where d is the spa-

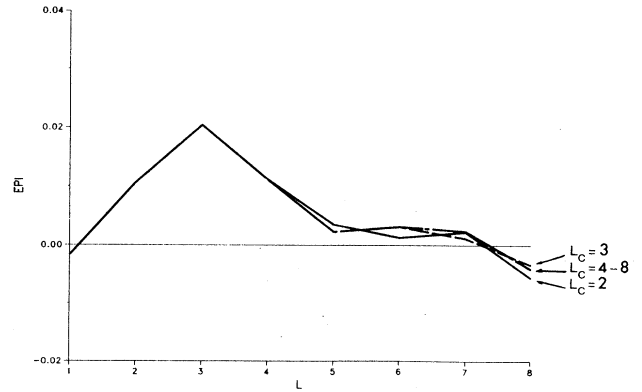


FIG. 3. Nearest-neighbor EPI (in arbitrary units) in the fcc structure for “3-8” values with $c_A=0.25$, as a function of the number of levels (L) with fixed cluster size. The cluster size is chosen so as to be exact for a given number of levels L_c . The results for $L_c=4-8$ are indistinguishable.

tial dimension. In particular, for $d=3$ this term is equal to $\tau L^3/6$ where τ is given by

$$\Delta^2(s_n) = \tau, \quad (3.1)$$

s_n is the number of sites in the shell n , and Δ^2 is the second-order finite-difference operator. For an fcc lattice with hopping parameters up to first or second neighbors, τ takes the values 20 and 36, respectively. For the bcc lattice with hopping parameters up to first, second, or third neighbors, the corresponding values are 12, 24, and 80, respectively. In order to use tight-binding parameters determined from *ab initio* calculations, it is necessary to include second-neighbor interactions in the fcc lattice and third neighbors in the bcc. This leads to a considerable increase in the size of the clusters used. Figure 3 reports results for the EPI of the ordered *AB* compound (with “3-8” parameters) on the fcc lattice with first and second neighbors, as a function of the number of levels and the size of the cluster used (with E_F and δ fixed at their values for 8 levels). The cluster size was determined by considering L_c exact levels for nearest- and next-nearest neighbor hopping. It can be seen that the results obtained with clusters exact for 4 to 8 levels are almost indistinguishable. This is confirmed in Table I, which contains results for the bcc lattice with third-neighbor in-

TABLE I. Position of the Fermi level for different “truncated” cluster sizes in the bcc lattice with third-neighbor interactions. The Fermi level E_F is computed for 8 exact levels of the continued fraction, with a cluster exact for L_c levels. Also given are the number of sites in each cluster and the computation time (in arbitrary units).

L_c	E_F	Sites	Time
2	0.682 12	192	255
3	0.683 69	538	417
4	0.684 44	1158	754
5	0.684 65	2132	1138
8	0.684 68	7978	1940

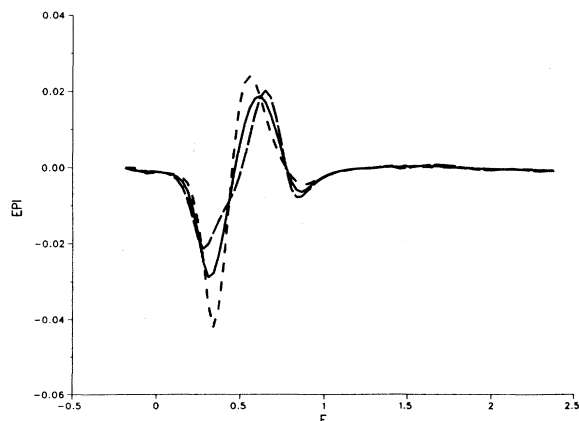


FIG. 4. Nearest-neighbor EPI (in arbitrary units) in the fcc structure for "3-8" values as a function of band filling, at concentration $c_A = 0.25$ (short-dashed line), 0.50 (solid line), and 0.75 (long-dashed line).

teractions. From this it can be concluded that the cluster size must be such as to guarantee $L_c/2$ exact levels, in the range of levels considered here (6–10). Using such a "truncated" cluster leads to an important gain in time: up to a factor of 4. Typically, the number of atoms in the cluster is around 600 (instead of 4000–8000).

Next, Fig. 4 shows the nearest-neighbor EPI for the "3-8" case in the fcc structure at three different concentrations as a function of band filling. These results were obtained by averaging over 10 configurations, using 8 levels in the continued fraction expansion. The number of nodes is in agreement with the values given by general theorems³⁶ and the curves have a similar overall shape, with a "phase-separating" region at the band edges and an "ordering" region near the center of the band (see also Ref. 17). By choice of the tight-binding parameters, the

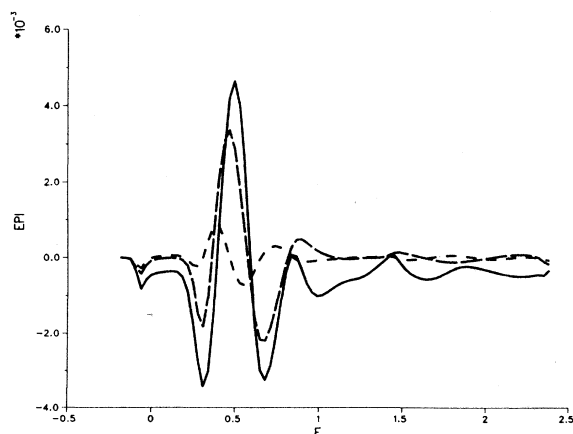


FIG. 5. Further-neighbor EPI (in arbitrary units) in the fcc structure for "3-8" values with $c_A = 0.25$ as a function of bandfilling; solid line, second neighbor; long-dashed line, third neighbor; and short-dashed line, fourth neighbor. Note the change in scale compared to Fig. 4.

local density of d states on a Rh and Ti site has a bandwidth between 0 and 1. For an energy above this band, the EPI, for any concentration, have very small amplitude. So that it can be concluded that the EPI are mainly related to the d orbitals. (This does not imply that the s and p orbitals are unimportant; for example, they certainly affect the shape of the EPI.) Also note that only the position of the first node is affected by changing the concentration. Pair interactions involving more distant atoms are plotted in Fig. 5. As expected, the number of nodes increases, while the magnitude of the EPI decreases, with increasing separation of the atoms involved (note the change in scale, compared to Fig. 4). To sum up, at this stage, it was found in agreement with previous results¹⁷ for d orbitals only, that configurational averaging converges quickly and that 10 configurations are

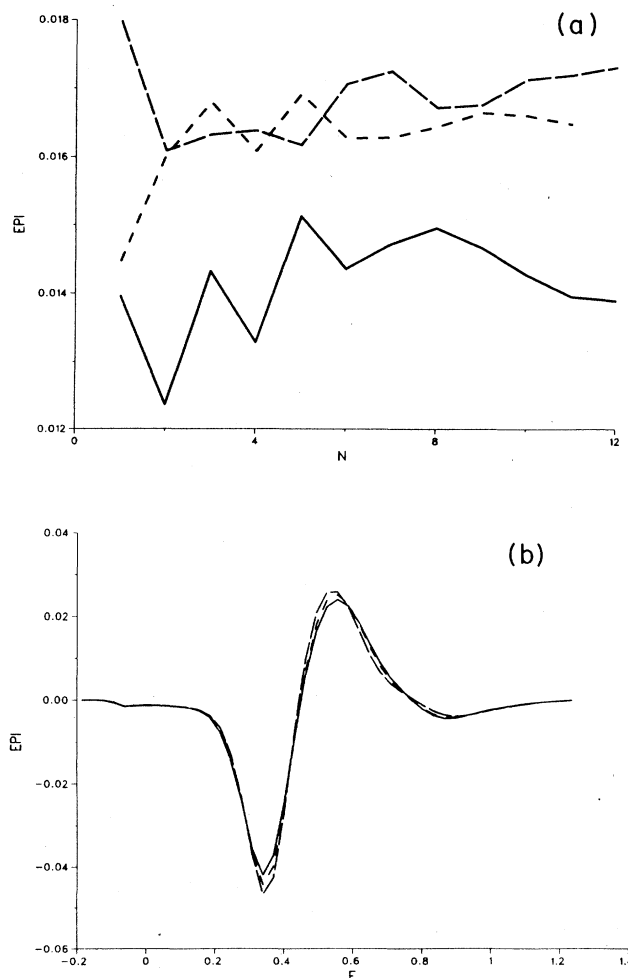


FIG. 6. Nearest-neighbor EPI (in arbitrary units) in the fcc structure for "3-8" tight-binding parameters with $c_A = 0.25$ for various prescriptions to generate the configurations (see the text): (a) as a function of the number of configurations (N), (b) as a function of bandfilling. Solid line: fixed concentration in every shell; short dashed line: fixed concentration in first shell; and long-dashed line: fixed overall concentration.

sufficient to obtain convergence. The number of levels is a crucial factor as far as computer time is concerned. Typically, a maximum of 8 levels is necessary and an important speedup can be obtained by using "truncated" clusters.

In order to study the influence of the environment on the EPI, three sets of configurations were generated. In the first one, the only constraint was the overall concentration of the recursion cluster, while in the second group the first coordination shell of the pair was also held at the fixed overall concentration, and in the third group this constraint was imposed in every concentric shell around the central pair. In all cases, adjustments were made by appropriate rounding of the shell occupancies to ensure that the total number of atoms was conserved. The resulting EPI are drawn as a function of the number of configurations (at a fixed concentration $c_A = 0.25$) in Fig. 6(a) and as a function of bandfilling (averaged over 12 configurations, for 8 exact levels of the continued fraction) in Fig. 6(b). Although the influence of the ordering constraints is clearly visible in Fig. 6(a), the differences are relatively small; a few percent between the first two cases, and approximately 20% in the case of concentric shells with constant compositions. It can be seen in Fig. 6(b) that the positions of the nodes are the same and only the extreme values are affected. Note also that the band filling selected corresponds to a Fermi level near the maximum in Fig. 6(b) so that deviations will be rather larger than on the average.

Next a group of calculations was performed for the binary alloy $\text{Rh}_c\text{Ti}_{1-c}$ with the orthogonal two-center tight-binding parameters tabulated by Papaconstantopoulos.²³ Figure 7 shows nearest-neighbor fcc and nearest- and next-nearest-neighbor bcc EPI as a function of concentration for this system. From these EPI one can determine the energy of mixing for the two structures as follows:²⁰

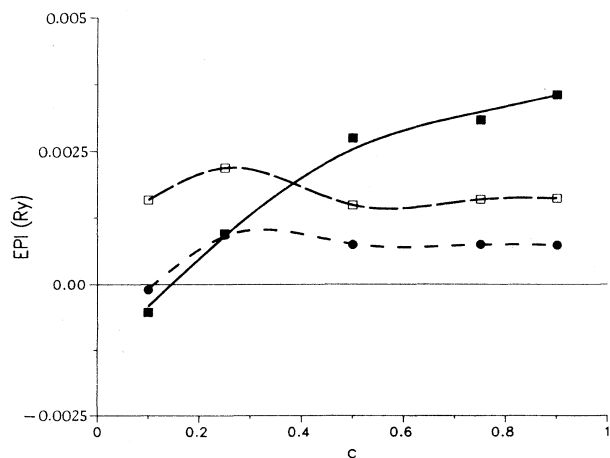


FIG. 7. EPI (in Rydbergs) for $\text{Rh}_c\text{Ti}_{1-c}$ as a function of the Rh concentration. Solid squares: nearest-neighbor EPI in the fcc structure; open squares: nearest-neighbor EPI in the bcc structure; and solid circles: next-nearest-neighbor EPI in the bcc structure. The curves are drawn to guide the eye.

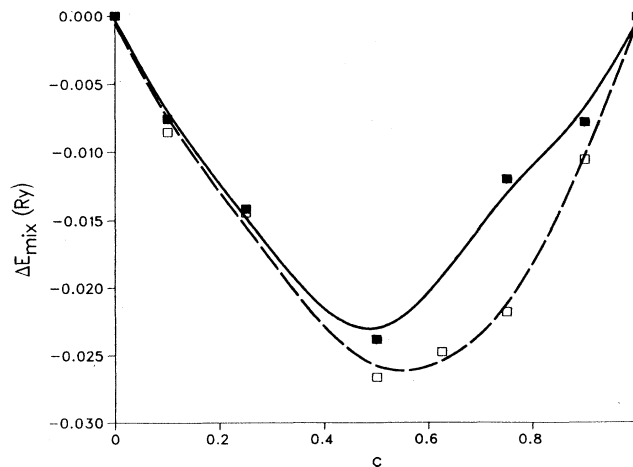


FIG. 8. Energy of formation of $\text{Rh}_c\text{Ti}_{1-c}$ in the bcc (upper curve) and fcc (lower curve) structure as a function of concentration.

$$\Delta E_m^I(c) = E_{\text{dis}}^I(c) - E_{\text{lin}}^I(c) + \Delta E_{\text{ord}}^I(c), \quad (3.2)$$

in which elastic and vibrational contributions, as well as volume changes, have been neglected. The different energy contributions involved are

$$E_{\text{lin}}^I(c) = (1-c)E_A^I + cE_B^I, \quad (3.3)$$

i.e., a linear interpolation between the cohesive energies of the pure elements in the crystal structure I , E_{dis}^I is the cohesive energy of the completely disordered state given in (2.34), obtained by configurational averaging of the band structure term (2.17), and ΔE_{ord}^I is the configurational part of the mixing energy, related to the EPI by

$$\Delta E_{\text{ord}}^I = \sum_h q_h V_h, \quad (3.4)$$

where V_h is the EPI between an atom and its h th neighbor and

$$q_h = \frac{1}{2}(cn_h^{BB} - c^2n_h), \quad (3.5)$$

where n_h is the coordination number and n_h^{BB} the number of BB pairs both corresponding to the h th neighboring site. The energy of formation defined as the difference $E_{\text{dis}}^I(c) - E_{\text{lin}}^I(c)$ corresponding to the EPI in Fig. 7 are shown in Fig. 8, for the bcc (upper curve) and fcc (lower curve) structure, respectively. As noted before, the calculation of the term $E_{\text{dis}}^I(c)$ must be performed very carefully. In (3.2) E_{dis}^I and E_{lin}^I are large numbers and their difference is very sensitive to the position of the Fermi level. In order to ensure sufficient accuracy, one can adopt the method discussed before, involving a small shift of the Fermi energy. The correction introduced by this small variation leads to a negligible change to the EPI (less than 0.01 eV). A phase diagram calculation using these results is in progress and will be reported upon elsewhere.

IV. SUMMARY AND CONCLUSIONS

This paper has addressed the calculation of effective-pair interactions in binary alloys, quantities that are essential to understand the statistical thermodynamics of these systems on a first-principles basis. It has been shown that these EPI can be calculated accurately and reliably by means of direct averaging over random configurations. To this end, the formalism set out previously¹⁷ has been extended in order to include s and p orbitals in a recursion method approach to a realistic tight-binding Hamiltonian. The feasibility of this scheme depends crucially on the use of the orbital peeling trick to calculate cohesive energy differences directly. Since no reciprocal-space transformation is made, the present method is ideally suited to treat problems with broken symmetry, such as partially ordered structures, or low-symmetric configurations, in particular surfaces and interfaces. For completely disordered systems, the results compare very well to those obtained within the coherent-potential approximation,¹⁷ although the present method is more time consuming since in the CPA only one recursive cycle needs to be performed once the effective medium is set up. On the other hand, since the configurational-averaging method repeats the same set of instructions for each random configuration, it is very well suited for parallel implementation on computers. It is also important to note that the present method takes ensemble averages (in an approximate way) of the appropriate physical quantities, rather than calculating these quantities for an "averaged" configuration. The former approach is of course the correct one in classical statistical mechanics.

The main difficulties in the present description of a disordered system arise because of charge transfer. They

involve a shift in the on-site energies and the determination of the Fermi level. Simple procedures to take these effects into account have been presented here, but further extensions are straightforward, if necessary. A considerable saving in computer time can be obtained by decoupling the number of levels from the number of atoms in the recursion cluster. Numerical simulations indicate that it is sufficient to take the number of atoms in the cluster appropriate for nearest-neighbor hopping parameters only, even if further neighbor interactions are present. A further conclusion of this work is that 10 configurations and a maximum of 8 levels are sufficient to guarantee an uncertainty of a few percent in the magnitude of the EPI. The main emphasis of the present paper has been on the formalism and general checks of convergence and other properties. Some preliminary results are included for the system $\text{Rh}_c\text{Ti}_{1-c}$, using the first-principles values obtained by a fit to an LAPW band structure. A further discussion of these EPI and the resulting phase diagram will be given in a forthcoming paper.

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