

## Local properties in the electronic structure of disordered binary alloys

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The electronic density of states (DOS) of disordered binary alloys is studied for a tight-binding model Hamiltonian, using a local approach based on a continued-fraction representation for the Green function. In addition to a single-site probability, a *short-range-order* parameter is introduced to monitor nearest-neighbor correlations. Our method employs a termination that allows for local fluctuations of both species of atoms, according to the configuration produced. The final DOS is obtained as a weighted average over all the local spectra generated in the way described above. We probe our approach in the one-dimensional case, and excellent agreement with Monte Carlo simulations is found.

### I. INTRODUCTION

The problem of disordered binary alloys, although exactly soluble in one dimension,<sup>1</sup> still poses many challenges to theorists in two and three dimensions. The exact methods developed for one-dimensional alloys are peculiar for their particular topology, and cannot be straightforwardly extended to higher dimensions. Efficient approximate schemes are then of great interest, specially if they also apply to higher-dimensional systems.

The coherent-potential approximation<sup>2</sup> (CPA) has been for many years the most widely used single-site method. Similarly to any mean-field theory, the qualitative trends are correctly described, but the bands and density of states obtained lack local properties and show no structure whatsoever.<sup>3</sup> In spite of the above fact, the idea of replacing the alloy by an *effective medium* (which self-consistently simulates the global properties of the system), has inspired a number of interesting contributions.<sup>4</sup>

In this paper we adopt a different point of view: we propose a non-self-consistent local approach based on the continued-fraction method.<sup>5</sup> The growth of a cluster is followed, counting the different possible configurations along with their probability of appearance. Site occupation is monitored by means of a long-range-order parameter that only depends on the concentration of both species (atoms *A* and *B*). In addition, a short-range-order parameter, which takes into account nearest-neighbor correlations, describes the alloy tendency to segregation or ordering (Cowley order parameter).<sup>6</sup> We have assumed *Markovian* short-range order, i.e., the probability distribution for configurations is completely determined by pair probabilities<sup>7</sup> parametrized by the Cowley parameter. This method is similar in spirit to Monte Carlo simulations, but not extremely large systems are needed and local properties are asymptotically exact.

Since the cluster size is limited by CPU time and memory, the continued fraction has to be terminated. This is a sensible step in the whole calculation, and different approaches can be devised to overcome this problem.<sup>8</sup> Physically, through the termination, one re-

places the real cluster environment by an effective medium, where the cluster is embedded. In our approach, the continued-fraction termination is given in terms of those for pure-*A* or pure-*B* systems. *Relative weights are ascribed according to the fraction of atoms of each component in the cluster configuration under study.* This procedure has to be contrasted with those where the termination is based on the virtual-crystal (VC) approach, with relative weights proportional to the global alloy concentrations.<sup>9</sup> In our treatment we assume that, for most probable configurations, a sufficiently large cluster is already a representative portion of the whole system. Within this sampling one assigns a larger weight to most probable configurations, and a smoother matching is attained using the above counting. Our method allows for exact solutions in cases such as segregation and the split-off limit. Monte Carlo computations for the disordered linear chain need large systems (of the order of  $10^4$  atoms) to get results of the same accuracy. Comparisons between both methods, as will be seen in the following sections, show excellent agreement in the global features as well as in the structures of the density of states. The computational work, for the method proposed in this paper, is iterative and can be efficiently implemented in small-size computers, with reasonable computer time. The above fact encourages extensions to systems of higher dimensions. Limiting cases, such as ordering, segregation, and band splitting, are correctly described within our approach.

In the following section we briefly discuss the model and the method of calculation. Numerical examples are then presented, and general conclusions are left for the final section.

### II. MODEL AND METHOD OF CALCULATION

The problem of order-disorder transitions in binary alloys is equivalent to an Ising model where the spin concentrations are kept constant.<sup>10</sup> If we label the atomic species as *A* and *B*, the site probabilities of finding an atom *A* or *B* are given by the concentrations  $c_A$  and  $c_B$ ,

respectively. In addition, correlations between nearest neighbors are monitored by pair probabilities  $p_{AA}$ ,  $p_{BB}$ ,  $p_{AB}$ , and  $p_{BA}$ , which exhaust all possible pairs. Normalization requires

$$p_{AA} + p_{BB} + p_{AB} + p_{BA} = 1 ,$$

$$p_{AA} + p_{AB} = c_A ,$$

$$p_{BB} + p_{BA} = c_B ,$$

which implies that we are left with only one free parameter. The usual choice is the so-called Cowley parameter,<sup>6</sup> which is defined as

$$\sigma = 1 - \frac{\frac{1}{2}(p_{AB} + p_{BA})}{c_A c_B} \quad (1)$$

and is limited to the range  $-1 \leq \sigma \leq 1$ . Special cases of interest are the following. (i) Ordering for  $c_A = c_B = 0.5$ , and  $\sigma = -1$ . This is equivalent to the antiferromagnetic Néel state. (ii) Segregation for  $\sigma = 1$ . The corresponding analog is the case of ferromagnetic domains. (iii) Random alloy, for which all pairs probabilities are the same. If  $c_A = c_B = 0.5$ , then  $\sigma = 0$ . It corresponds to the disordered paramagnetic case.

To study the electronic properties, we model our system through a tight-binding Hamiltonian with diagonal disorder:

$$\mathcal{H} = \sum_i \varepsilon_i |i\rangle \langle i| + \sum_{i \neq j} V_{ij} |i\rangle \langle j| , \quad (2)$$

where the diagonal element  $\varepsilon_i$  is  $\varepsilon_A$  or  $\varepsilon_B$ , and  $V_{ij} = V$  for all pairs of nearest neighbors. In (2), the states  $\{|i\rangle\}_i$  are Wannier orbitals centered at the  $i$ th site of the lattice. Within this representation, matrix elements of the Green function are given by

$$\mathcal{G}_{ij}(E) = \langle i | (E - \mathcal{H})^{-1} | j \rangle , \quad (3)$$

and the local DOS at the origin (site 0) is

$$\begin{aligned} n(E) &= -\frac{1}{\pi} \text{Im} \mathcal{G}_{00}(E + i0^+) \\ &= -\frac{1}{\pi} \text{Im} \langle 0 | (E + i0^+ - \mathcal{H})^{-1} | 0 \rangle . \end{aligned} \quad (4)$$

In formulas (4),  $0^+$  stands for a small positive imaginary part of the energy, which warrants the correct analytic properties of the retarded Green function. This small term transforms the imaginary part of the poles from  $\delta$  functions to Lorentzians, thus giving a dispersion to the DOS. The matrix element  $\mathcal{G}_{00}$  may also be represented as a continued fraction according to standard techniques:<sup>5</sup>

$$\mathcal{G}_{00}(E) = \frac{1}{E - a_0 - \frac{b_1^2}{E - a_1 - \frac{b_2^2}{E - a_2 - \dots}}} , \quad (5)$$

where the  $a$  and  $b$  coefficients are obtained through the recursive *chain model* of Haydock:<sup>5</sup>

$$b_{n+1} |n+1\rangle = \mathcal{H} |n\rangle - a_n |n\rangle - b_n |n-1\rangle . \quad (6)$$

The initial state  $|0\rangle$  is just  $|0\rangle$ , the Wannier state at the origin. All the other states are generated recursively by means of Eq. (6), and the Hamiltonian is three-diagonal in the base  $\{|v\rangle\}_v$ . For a tight-binding Hamiltonian with nearest-neighbor hopping, the latter basis involves successive shells of neighbors, in such a way that carrying the recursive process to the  $n$ th order means to study a cluster of  $(2n+1)$  atoms for the one-dimensional case. It is worth mentioning that our procedure follows strictly Haydock's method, and that all states are generated through the complete Hamiltonian itself, as it is usually done when dealing with a chain model. We have not attempted to use the modified method developed by Jacobs,<sup>9</sup> where a different orthonormalized basis is obtained by applying, in mixed form, the diagonal and off-diagonal parts of the Hamiltonian.

For a pure system all the coefficients in the continued fraction (5) are constant, and the Green function can be obtained self-consistently solving an equation of second degree. A localized impurity, or a finite cluster, can be characterized by a finite number of different coefficients and an infinite tail corresponding to a constant chain. We can think of a disordered chain in a similar form, looking at the different configurations of a finite cluster (as big as one can calculate), and simulating an infinite tail where the cluster is attached. In our case, as mentioned in the Introduction, we terminate the continued fraction by matching a termination of the form

$$T = f_A T_A + f_B T_B , \quad (7)$$

where  $f_A$  and  $f_B$  are the fractions of atoms  $A$  or  $B$  present in the cluster under study. The quantities  $T_A$  and  $T_B$  are the termination for a pure  $A$ - or  $B$ -like system, respectively. One can calculate the probability of the occurrence of a given cluster, using the concepts summarized at the beginning of this section. The average Green function is obtained here as a weighted sum over all individual cluster Green functions, and is independent of the choice of the origin. Our procedure allows for statistical fluctuations in the termination, since we count the respective fractions of atoms at any instance. As will be seen in the following section, this method appears as extremely promising when compared to Monte Carlo simulations. We will also compare our procedure with a virtual-crystal-like termination for the Green function

$$T = c_A T_A + c_B T_B , \quad (8)$$

where  $c_A$  and  $c_B$  are the concentrations. While this latter approach seems to work with the same efficiency in the random case, it fails in reproducing situations near segregation and near the complete split-off limit, even for extremely large clusters.

### III. EXAMPLES CALCULATED

We essentially study two cases: one with overlapping bands, and the other with bands sufficiently apart to see band splitting. Different values of the Cowley parameter  $\sigma$  were investigated, in the whole range  $-1 \leq \sigma \leq 1$ . Depending on the concentration,  $\sigma$  may assume different limiting values, as it is apparent from formula (1). We

have compared all our results with Monte Carlo simulations based on Dean's method<sup>11</sup> for a disordered alloy with  $10^4$  atoms. In our approach we attain up to the  $n=8$  iterative process, which means that we study all the configurations of a cluster of  $2n+1=17$  atoms. The process itself may be substantially reduced if one cuts configurations with a small probability of occurrence. This procedure will be adopted for higher-dimensional systems in future works.

We also study the resolution of our results with the imaginary part of the energy,  $\delta\epsilon$ , and with the number of points in the energy interval. Normalizing the energy in units of  $V$ , the hopping constant, we found that  $\delta\epsilon=10^{-4}$  was an optimum value, in the sense that no important structures were concealed, and the computer time was kept within reasonable limits.

The number of points in the energy interval was also tested, showing no marked differences when we increased this number from 200 to 800. Taking this fact into account, we employ 400 points as a *bona fide* value for all examples. For the one-dimensional case it is known that all states are localized,<sup>12</sup> even for small disorder, and ultimately one should obtain a density of states that is a set

of  $\delta$  functions with a support of zero measure. In practice, for numerical computations, one never realizes the above condition, since  $\delta$  functions are transformed into peaks of finite width when a small imaginary part of the energy is introduced.

Figure 1 is a sequence showing how the iterative process works, and the final result is compared with a Monte Carlo calculation. We see there that the essential features of the DOS are already present at the stage of  $n=4$  (a cluster of nine atoms and eight exact moments). This example corresponds to the random case ( $\sigma=0$ ), with concentration  $c_A=0.5$ . A remarkable correspondence can be established with all the structures (peaks, singularities, antiresonances, bandwidth, etc.) obtained through Monte Carlo simulations.

In Fig. 2, we keep the concentrations fixed and vary the Cowley parameter over the whole range permitted, from tendency to ordering ( $\sigma=-1$ ), to segregation ( $\sigma=1$ ), passing through the random case ( $\sigma=0$ ). For  $\sigma=-1$ , the alloy is ordered, the sequence  $\cdots ABABAB \cdots$  being the only possible configuration. In this case we see the appearance of a gap

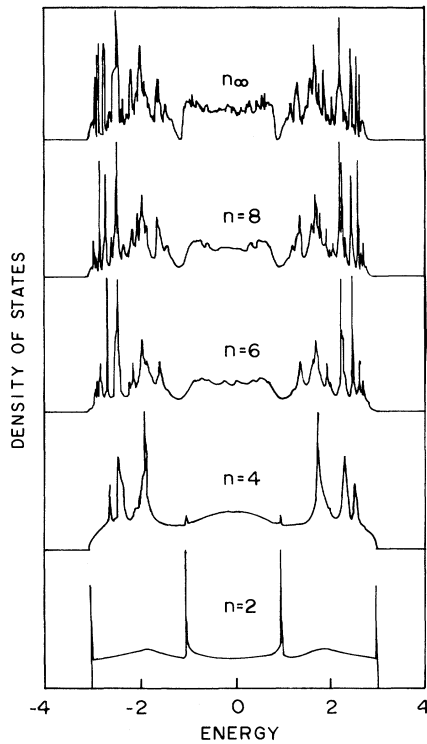


FIG. 1. DOS for the random case ( $\sigma=0$ ), with equal concentrations  $c_A=c_B=0.5$ . Energy is given in units of  $V$ , the hopping matrix element. Individual band centroids are located at  $\epsilon_A=-1$  and  $\epsilon_B=1$ , with band overlapping in the whole range  $-1 \leq \epsilon \leq 1$ . The calculations shown in the figure have been carried down to the  $n=8$  iterative process with 400 points in the energy interval. The figure displays the ascending sequence for  $n=2, 4, 6$ , and 8 iterations, and all the cases are compared with the Monte Carlo simulation (upper part).

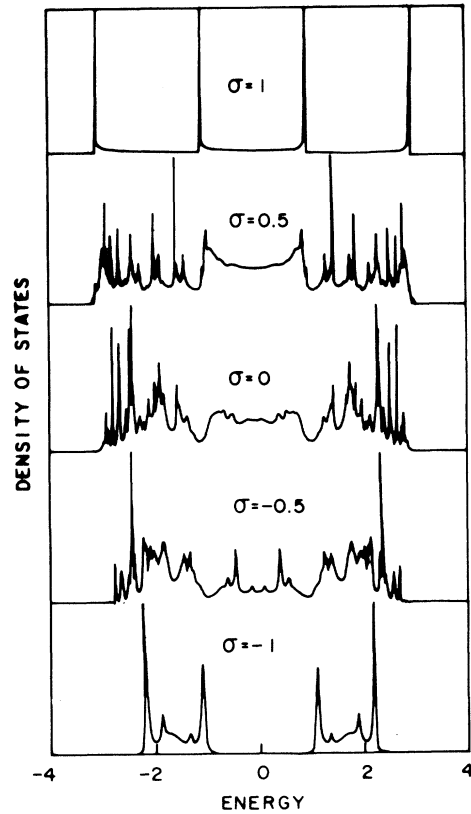


FIG. 2. This sequence shows changes in the DOS when the correlation parameter  $\sigma$  is varied. Figures are obtained with  $n=8$  and  $c_A=c_B=0.5$ , while  $\sigma=-1, -0.5, 0, 0.5$ , and 1 in ascending order. For the ordered case ( $\sigma=-1$ ), the extra periodicity obtained when we double the unit cell yields a gap at the center of the band. This region begins to be populated when we vary  $\sigma$  in the direction to the segregated alloy (upper part of figure).

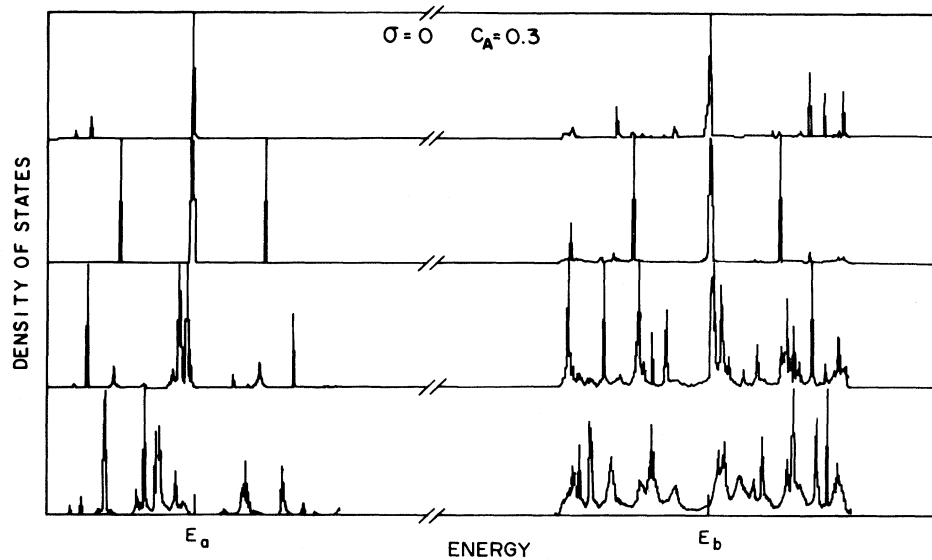


FIG. 3. Split-off regime displaying both majority and minority subbands for concentrations  $c_A=0.3$  and  $c_B=0.7$ , for a random alloy ( $\sigma=0$ ). The band centroid for the minority subband is kept fixed, while the other centroid is slid apart with values  $\epsilon_B=3, 9, 49$ , and  $99$ , when going up in the figure.

due to the extra periodicity of the lattice. In contrast, for  $\sigma=1$ , we obtain simple superposition of two pure band structures, which corresponds to the segregated alloy. Big changes are developed when the correlation parameter  $\sigma$  is varied. These examples may correspond to real cases with different atomic species, or to samples prepared by using different methods, such as quenching or heat treatment.

Up to now, all the cases depicted correspond to overlapping bands, with single-site energies at  $-1$  and  $1$ , in units of  $V$ . In Fig. 3, we display a different sequence, where the concentrations and the short-range-order parameter are fixed, but we vary the relative position of band centroids. The lower case corresponds to tangent bands, one centered at  $\epsilon=-1$  and the other at  $\epsilon=3$ , and the upper one to the complete split-off case, when one of the bands has been taken to infinity (for the calculation we use  $\epsilon_B=99$ ). This type of picture, with neat peaks corresponding to one-atom clusters and two-atom clusters for the minority band, will be extremely difficult to reproduce using a nonlocal approach.

Finally, we would like to compare our method with the one that employs a virtual-crystal termination given by (8). In Fig. 4 we display the random case for equal concentrations, at stages  $n=2,4$ . There are marked differences for the three-atom cluster (absence of any structure in the VC case), but both DOS's are extremely similar already at the stage  $n=4$ . For larger clusters no differences can be detected. We encounter a different situation near segregation or near the split-off limit. In Fig. 5 we show the complete sequence up to  $n=8$  (17-atom cluster) using the virtual-crystal termination for the segregated limit with equal concentrations. All the cases are compared with the exact result, which is shown in the uppermost graph. Spurious structures are still seen, even

in the  $n=8$  case. In contrast, we note that our method already reproduces the exact result at the stage  $n=2$ . In Fig. 6, we compare both methods for the split-off example of Fig. 3. While our approach clearly yields the atomic

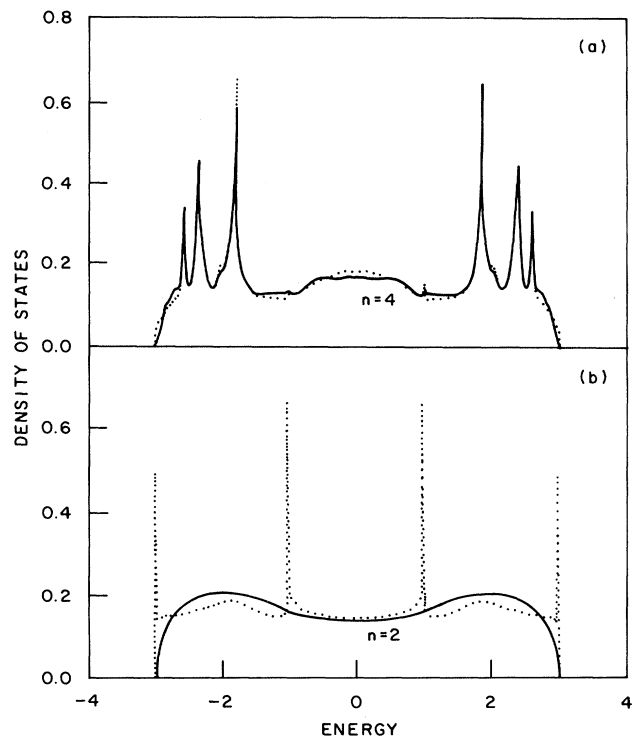


FIG. 4. Comparison between our method (dotted line) and the VC approach (solid line), for the stages  $n=2$  and  $4$ , for the example depicted in Fig. 1 ( $\sigma=0$  and  $c_A=c_B$ ).

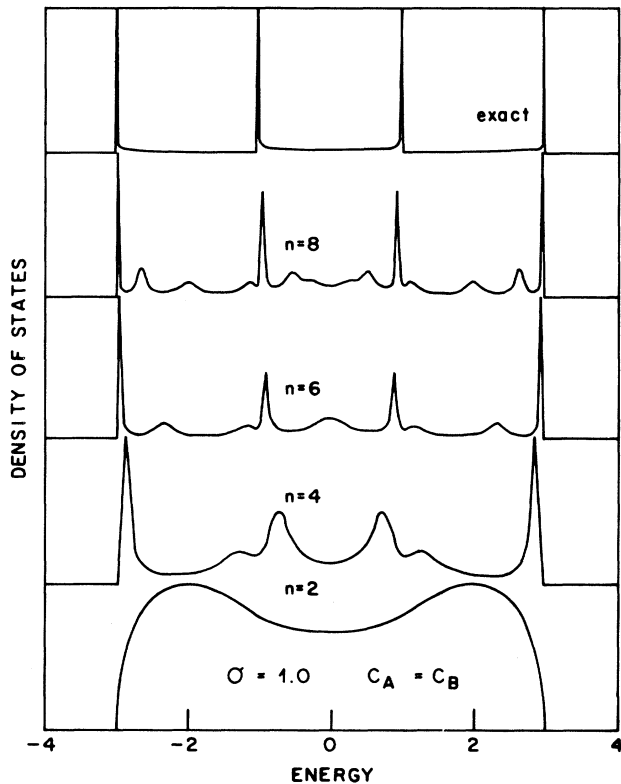


FIG. 5. Complete sequence for the segregated case using the VC termination. For comparison, we are also showing the exact result in the uppermost part of the figure (it has been obtained using our method with  $n=2$ ). The VC termination simulates a medium with mean alloy properties, thus producing a mismatch at the surface of the cluster.

limit with very small resonances, the VC termination presents spurious states in the middle of the energy interval. Those states, as well as the structures of Fig. 5, are produced by the mismatching with the termination.

On the other hand, modified CPA calculations to include local effects lead to highly nonlinear self-consistent equations, with the introduction of several coherent potentials (White and Economou, Ref. 4). The numerical methods are then much more involved than those used in our simple approach.

#### IV. CONCLUSIONS

A local treatment for the DOS of disordered alloys has been presented. Our method employs Haydock's scheme, where the Green function is represented by an infinite continued fraction, which in actual numerical computations is cut to a certain order. The DOS, for a finite continued fraction, is a sequence of weighted  $\delta$  functions. A termination is necessary, through the introduction of an effective self-energy, which also assures some analytical properties of the Green function. We can also give a physical interpretation of the above procedure.

(i) The study of a finite cluster yields a finite continued fraction for the Green function. In Haydock's iterative procedure, one includes in a hierarchical way the role of successive shells of neighbors. Our basis is generated by means of formula (6), through the action of the complete Hamiltonian (2), the latter being strictly *three-diagonal* in the above representation. Our results show that, for a sufficiently large cluster ( $n=6$  or  $8$ ) the finite basis thus generated is *close* to completeness, and a smooth matching with the termination can be achieved. We do not

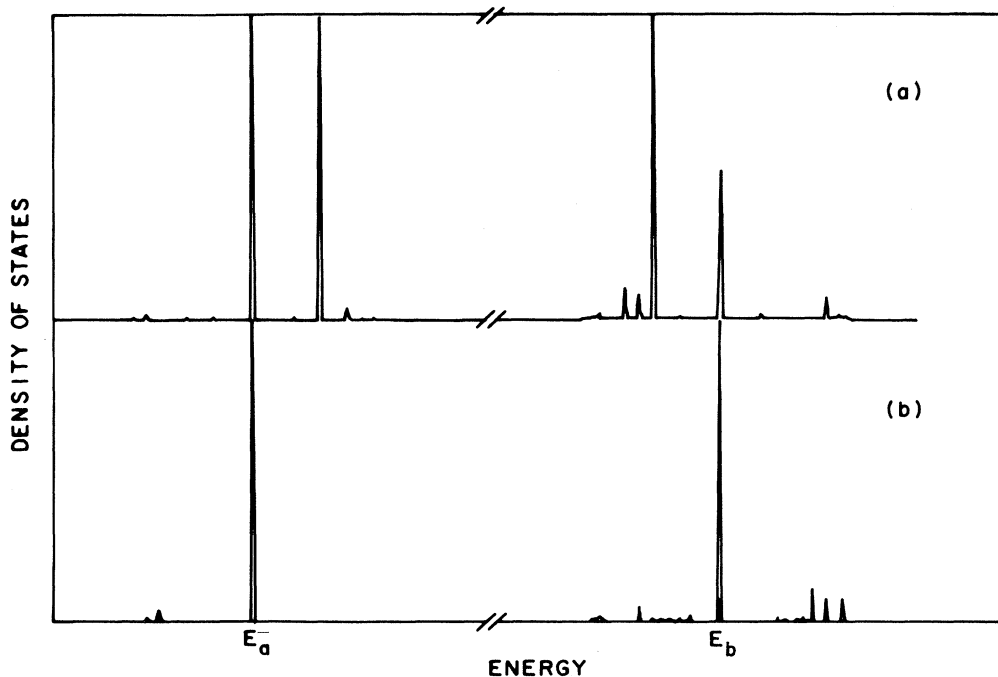


FIG. 6. The split-off limit for the same example of Fig. 3 ( $\sigma=0$  and  $c_A=0.3$ ), with the VC calculation shown in the upper part. VC termination generates spurious states between both atomic levels.

need to recur to more elaborate procedures for eliminating spurious states produced at the surface of small clusters. For a given configuration and up to the eighth iterative process, we warrant 16 exact moments for the DOS. Since the total DOS is obtained as a weighted superposition over configurations, we expect the same number of exact moments in the final result.

(ii) A termination with an effective self-energy simulates an *effective medium* where the above cluster is connected. The medium should contain an *average* amount of information of the disordered alloy. Obviously, this latter procedure is not unique. We are proposing here a method that allows for local fluctuations in cluster statistics.

Particularly important cases, such as ordering, segregation, and the complete split-off bands, can be obtained within our scheme in a direct manner. Our method is especially well suited for dealing with the latter, when the separation between bands is much bigger than the bandwidth. In this case, the transfer of electrons from atoms of one type to the other appears as an extremely improbable event, since the energy involved in the process is very high (atoms of the other type form perfect barriers). The DOS displays a series of peaks typical of *localization phenomena*,<sup>13</sup> which are related to small clusters of alike atoms surrounded by atoms of the other species (in the

random case, for equal concentrations, the picture is symmetric for both types of atoms). We also obtain other peaks that do not correspond to localized clusters of atoms, but represent scattering resonances introduced by tunneling through the high, but not infinite barriers.<sup>13</sup> The latter effect disappears for the minority band, as long as the concentration decreases. This picture is difficult to be reproduced if a nonlocal approach is adopted.

Concerning localization, more interesting phenomena are displayed by the two-dimensional case, where clusters can percolate along well-defined directions and be localized for others. A richer taxonomy of extended and localized states permitted by the new topology is thus obtained.<sup>13</sup>

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