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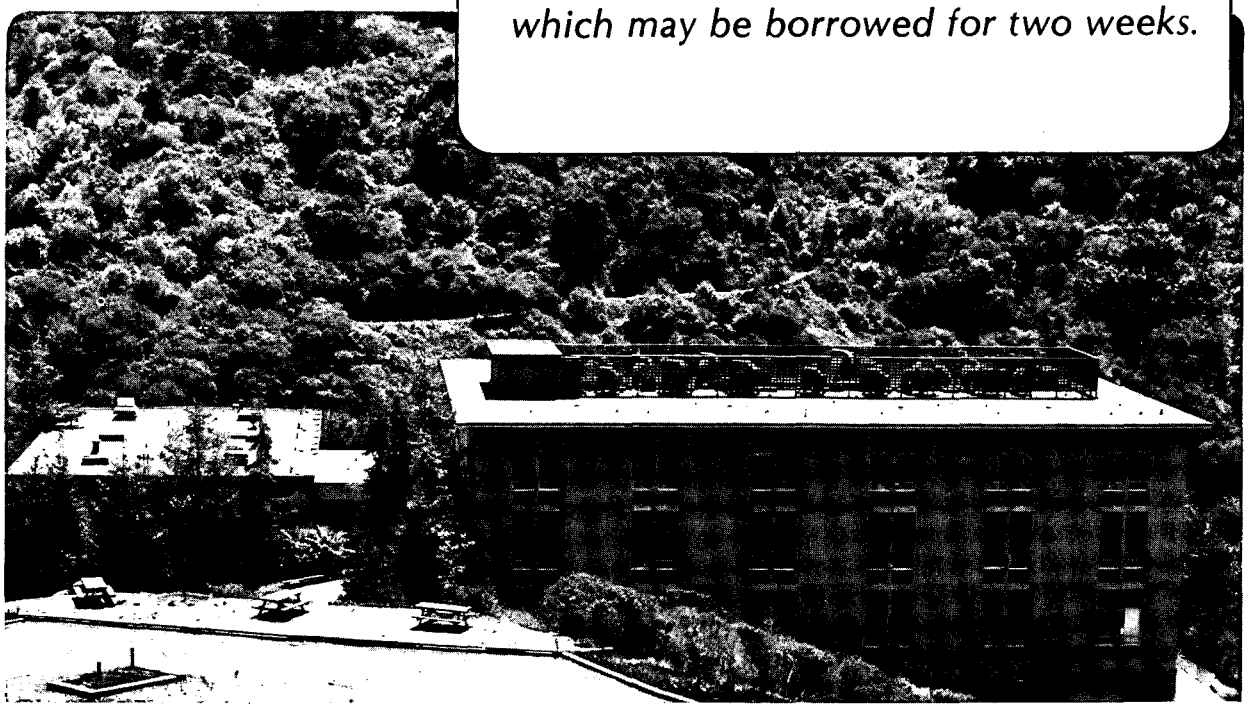

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Abstract It is shown that effective pair interactions (EPI) in disordered binary alloys can be calculated accurately and reliably by direct averaging over a small number of randomly selected configurations within the framework of the recursion method. This approach is illustrated on a canonical tight-binding Hamiltonian and relies on the 'orbital peeling' technique to calculate energy differences directly, without large subtractive cancellations. The results are checked for convergence, both as a function of the number of configurations and the number of levels of the continued fraction, and are also compared with more elaborate calculations. The main advantages of such a real-space method are the computational simplicity and the possibility to treat deviations from lattice periodicity. The EPI are basic quantities to understand the phase formation and stability of substitutionally disordered solid solutions.

The calculation of temperature-composition alloy phase diagrams from first principles is a problem that has important applications for materials design and, at the same time, poses fundamental questions about the nature of disordered quantum systems [1]. This task involves two steps : a quantum mechanical determination of the interactions in the solid, and a minimisation of the free energy expression obtained by the techniques of statistical mechanics. Both have to be performed at a high level of precision, since otherwise unrealistic results may be found, and it is only very recently that such schemes have been implemented [2]. The most successful treatments of the statistical mechanical problem, like the Monte Carlo [3] and Cluster Variation Method [4], express the alloy free energy in terms of effective cluster interactions (ECI). Several methods have been developed for calculating these parameters *ab initio*. Connolly and Williams [5] used an inversion scheme starting from total energy local density calculations for the *ordered* compounds to determine pair and cluster interactions for the disordered system. Alternatively, one can perturb the *completely disordered* alloy, modeled through an appropriate effective medium, following the Generalised Perturbation Method (GPM) of Ducastelle and Gautier [6] or the Embedded Cluster Method of Gonis and co-workers [7]. Thus, all of these methods restore the lattice periodicity before the ECI are calculated and cannot be easily extended to handle systems with broken translational symmetry. Here it is proposed to calculate 'alloy' parameters by averaging ECI obtained for a number of randomly generated configurations (at fixed concentration). This real-space approach has the advantage, apart from its conceptual simplicity, that no symmetry requirements need to be imposed. In particular, short- or long-range order can be included in a completely straightforward way. In addition, the coherent potential approximation (CPA), although providing a very satisfactory description of random metallic alloys in general, still an approximation, is circumvented.

The idea of configurational averaging of local operators is a very natural one and has been used in the past to determine a variety of physical properties (see [8], and references therein). The feasibility of such an approach depends essentially on the rate of convergence

as a function of the number of configurations. For the local density of states on a central atom, it is necessary to perform an exact average over the first shell of neighbours [9]. This involves 144 inequivalent configurations for the fcc lattice and is too time consuming for many applications. On the other hand, the ECI behave like cohesive energy differences, i. e. integrated quantities, and may therefore be expected to converge more quickly. The recursion method [10], applied to a tight-binding Hamiltonian, provides a very convenient algorithm to implement this approach. Moreover, the 'orbital peeling' trick, developed by Burke [11] within this formalism, allows for a direct calculation of cohesive energy differences, so that no numerical instabilities due to subtractive cancellation occur, a prerequisite for the feasibility of the present approach.

The purpose of the present paper is to show that configurational averaging for ECI calculations converges quickly and leads to good agreement with CPA results. To this end a number of simplifying assumptions has been made, without affecting the validity of the conclusions. The present work is only concerned with binary alloys A_cB_{1-c}. A basis of five d orbitals per atom is considered, together with canonical values for the tight-binding parameters. This is a reasonable approximation for transition metal alloys and quite capable of producing realistic phase diagrams [12]. Moreover, s- and p-orbitals can be readily included in this formalism, the main complication being the requirement of charge self-consistency, as will be discussed in a forthcoming publication [13]. The recursion method considers essentially a finite cluster of atoms, corresponding to a number of shells around a central atom, equivalent to the number of levels in the continued fraction expansion for the Green's function. To eliminate boundary effects, or equivalently, to ensure that the Green's function possesses the correct singularities, one needs to construct a terminator for the continued fraction. This subject has been discussed extensively ([14,15] and references therein) and its use for ECI calculations is investigated here in some detail.

Often the most important ECI is an effective pair interaction (EPI), defined as [1]:

$$E_{pq} = \frac{1}{4}\langle V_{AA}^{\sigma} + V_{BB}^{\sigma} - V_{AB}^{\sigma} - V_{BA}^{\sigma} \rangle, \tag{1}$$

where the averaging is over all possible configurations σ at a given concentration, and V_{IJ}^{σ} is the total energy for the particular configuration σ with atomic species I and J at sites p and q respectively. In the random alloy, V_{IJ}^{σ} is reduced to solely the band structure contribution, because of a cancellation of terms [16]. The electronic properties are obtained from a general tight-binding Hamiltonian :

$$H_{IJ}^{\sigma} = \sum_{n,\lambda} |n,\lambda\rangle \varepsilon_n^{\lambda} \langle n,\lambda| + \sum_{n \neq m,\lambda\mu} |n,\lambda\rangle \beta_{nm}^{\lambda\mu} \langle m,\mu|, \tag{2}$$

where $|n,\lambda\rangle$ is the atomic orbital of symmetry λ centered at the site n, ε_n^{λ} is the on-site energy, assumed to depend only on the nature of the atom at site n (thus only taking values ε_A and ε_B) and $\beta_{nm}^{\lambda\mu}$ is the hopping parameter, similarly restricted to one of three values β^{AA}, β^{BB} or β^{AB}. The first two are related to the two-center integrals for the pure metals : $dd\sigma$, $dd\pi$ and $dd\delta$ in the Slater-Koster [17] parametrisation scheme, while the hopping parameter β^{AB} is taken to be the geometric mean of β^{AA} and β^{BB} (Shiba [18]). Introducing the Green's function at complex energy z :

$$G_{IJ}^{\sigma} = (z - H_{IJ}^{\sigma})^{-1}, \tag{3}$$

the EPI can be written as :

$$E_{pq} = \langle -\frac{1}{4} \int^{E_F^{\sigma}} \mathrm{Im}\, Z^{\sigma}(E)\, dE \rangle, \tag{4}$$

where E_F^{σ} is the Fermi level and $Z^{\sigma}(E)$ the generalised phase shift :

$$Z^{\sigma}(E) = -\frac{1}{\pi} \ln \det \frac{G_{AA}^{\sigma} G_{BB}^{\sigma}}{G_{AB}^{\sigma} G_{BA}^{\sigma}}. \tag{5}$$

The operation involved in the definition of the EPI is an exchange of atoms on sites p and q. Since this is a localised perturbation the size of the determinant in (5) is finite. Furthermore,

assuming that the subblock of the Hamiltonian relative to all atoms except those at sites p and q is unaltered under this exchange, the orbital peeling method [11] provides an efficient means to obtain the phase shifts. This entails calculating the diagonal elements of the upper IJ block of the four Green's functions in (5). Although the matrices G_{IJ} have the size 2n, n being the number of orbitals per site, one needs to compute only determinants of size n, because of cancellations. This formalism will be presented in more detail in a longer paper [13].

In the present work canonical parameters are used : $dd\sigma = -0.5$, $dd\pi = 0.25$, $dd\delta = 0$. and the on-site energies are related to the diagonal disorder parameter :

$$\delta = \frac{\varepsilon_B - \varepsilon_A}{W}, \tag{6}$$

where W is the bandwidth for the alloy, that is the concentration weighted mean of the pure element bandwidths. Thus all energies can be expressed in bandwidth units (b.u.).

First it is necessary to investigate the rate of convergence as a function of the number of configurations and the number of recursion levels. Typical results are plotted in Fig. 1, which shows the nearest neighbour EPI in the fcc structure as a function of N, the number of configurations over which the averaging was performed, and for various numbers of levels (L). The diagonal disorder parameter used was $\delta = 0.8$ and the concentration $c = 0.70$. It should be pointed out that, as the number of levels was changed, the same set of configurations was used, to allow for a direct comparison of the results. From this figure, and many more that were calculated [13], one concludes that the EPI's converge quickly in all cases and that the uncertainty after 20 configurations is less than 1 %. Fig. 2 shows a comparison of the same data, obtained after 10 configurations (full line) and after 20 configurations (dashed line), as a function of the number of levels. Clearly, improved accuracy is obtained by increasing the number of levels - rather than the number of configurations. Phase diagram calculations [2,12] typically use $L = 4$ or 5, since for larger L-values the computation becomes very time consuming. From the results in Fig. 2 it can be estimated that

this gives an uncertainty of about 4 %. Similar conclusions were also found to hold for ECI involving more distant neighbours or larger clusters.

Having established that the proposed scheme converges satisfactorily, it is important to compare the results with those obtained by the CPA-GPM. This comparison is shown in Fig. 3, again for an fcc lattice with $c = 0.70$ and diagonal disorder $\delta = 0.80$. Plotted is the nearest neighbour EPI as a function of bandfilling N_e. The full line shows the results obtained by averaging over 20 configurations and the dashed line is the CPA-result. In both cases 15 levels were used in the continued fraction expansion for the Green's function. As seen, the asymmetry, nodes and central peak height agree closely, but the width of the clustering region is slightly smaller when calculated by configurational averaging. The main discrepancy arises at the band edges, where the perturbation series in the GPM may be converging more slowly. The same trends were confirmed for other concentrations and δ-values.

Finally, the termination of the continued fraction will be discussed. The size of the cluster needed for a calculation of L exact levels of the continued fraction grows as L^d, d being the spatial dimension [19]. Consequently only a limited number of levels can be determined exactly and different prescriptions ([14,15] and references therein) have been proposed to terminate the continued fraction. When there are no band gaps, the simplest approach is the quadratic terminator, which amounts to putting all recursion coefficients a_i, b_i $(i > L)$ equal to a_L, respectively b_L. Without a terminator, one obtains for real energies a set of delta functions and integrating such quantities leads to discontinuous curves. Fig. 4 shows the values obtained for the nearest neighbour EPI (for $\delta = 0.75$ and $c = 0.70$) as a function of bandfilling with the quadratic terminator (long-dashed line), and those without a terminator (full line). The latter quantities can be determined by a sum over poles and zeros of the Green's function in the complex energy plane. With the exception of the central extrema, the agreement between these two curves is good. To avoid the discontinuous nature of such quantities integrated up to the Fermi level, Burke [11] has proposed to add to the computed

set of levels $\{a_i, b_i; i = 1, ... L\}$, one level such that $a_{L+1} = E_F$, thus guaranteeing that the curves as a function of bandfilling are continuous. In Fig. 4 the short-dashed line represents the EPI obtained by this method of fixed nodes. Although the general shape is the same as in the other curves, there are significant discrepancies, in particular in the magnitude of the EPI. The same trend, a systematic underestimation, was observed for all cases that were calculated. This result can be understood by the following argument. Nex [20] has determined exact upper and lower limits for any integrated quantity obtained from the Green's function. Without terminator, the calculated value will be a staircase function and alternate between these limits. The fixed node method amounts to taking the arithmetic mean of the two limits. In the determination of the EPI one adds and subtracts such curves and therefore discrepancies will be amplified. Moreover, the poles and zeros of the four continued fractions are different and thus the 'exact' EPI are not expected to oscillate around the medium line. Burke [11] estimated the error induced by fixing a node at the Fermi level to be of the order of 15 %. In the present case, the results show that these errors may be larger and depend strongly on bandfilling.

In conclusion, it has been shown that configurational averaging of EPI converges rapidly and compares very well with CPA-GPM results. The method has been illustrated here on a canonical tight-binding Hamiltonian, but is easily extended to the case of realistic tight-binding parameters including s- and p-orbitals [13]. This approach is physically transparent and computationally efficient. An additional advantage is the possibility to treat the off-diagonal disorder exactly, rather than by Shiba's prescription [18], if a value for the hopping parameter β^{AB} is known. Moreover, since the theory is formulated in real space it is ideally suited to treat deviations from the lattice periodicity, such as partially ordered or low-symmetric systems, in particular surfaces and interfaces with or without defects (work in progress). The question of the termination of the continued fraction has been addressed and it is concluded that the simple quadratic terminator is actually the best choice in the present scheme. The rapid convergence of configurational averaging for the determination of ECI

came as a surprise, even to the authors. In retrospect, its success must be attributed to two factors : the fact that ECI are integrated quantities, less sensitive to local perturbations and the use of orbital peeling to calculate energy differences directly.

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Figure Captions.

Fig. 1 Nearest neighbour effective pair interaction in the fcc structure as a function of the number of configurations that is averaged, for various numbers of levels L in the continued fraction expansion of the Green's function. The same set of random configurations was used for different L-values. The EPI are expressed in bandwidth units (b.u.).

Fig. 2 Nearest neighbour EPI averaged over 10 configurations (full line) and over 20 configurations (dashed line) as a function of the number of levels.

Fig. 3 Nearest neighbour EPI as a function of bandfilling as obtained by configurational averaging (full line) and by the CPA-GPM method (dashed line).

Fig. 4 A comparison of different terminators for the continued fraction. Full line : method of poles and zeros; long dashed line : quadratic terminator; short dashed line : method of fixed nodes. Plotted is the nearest neighbour EPI as a function of bandfilling.

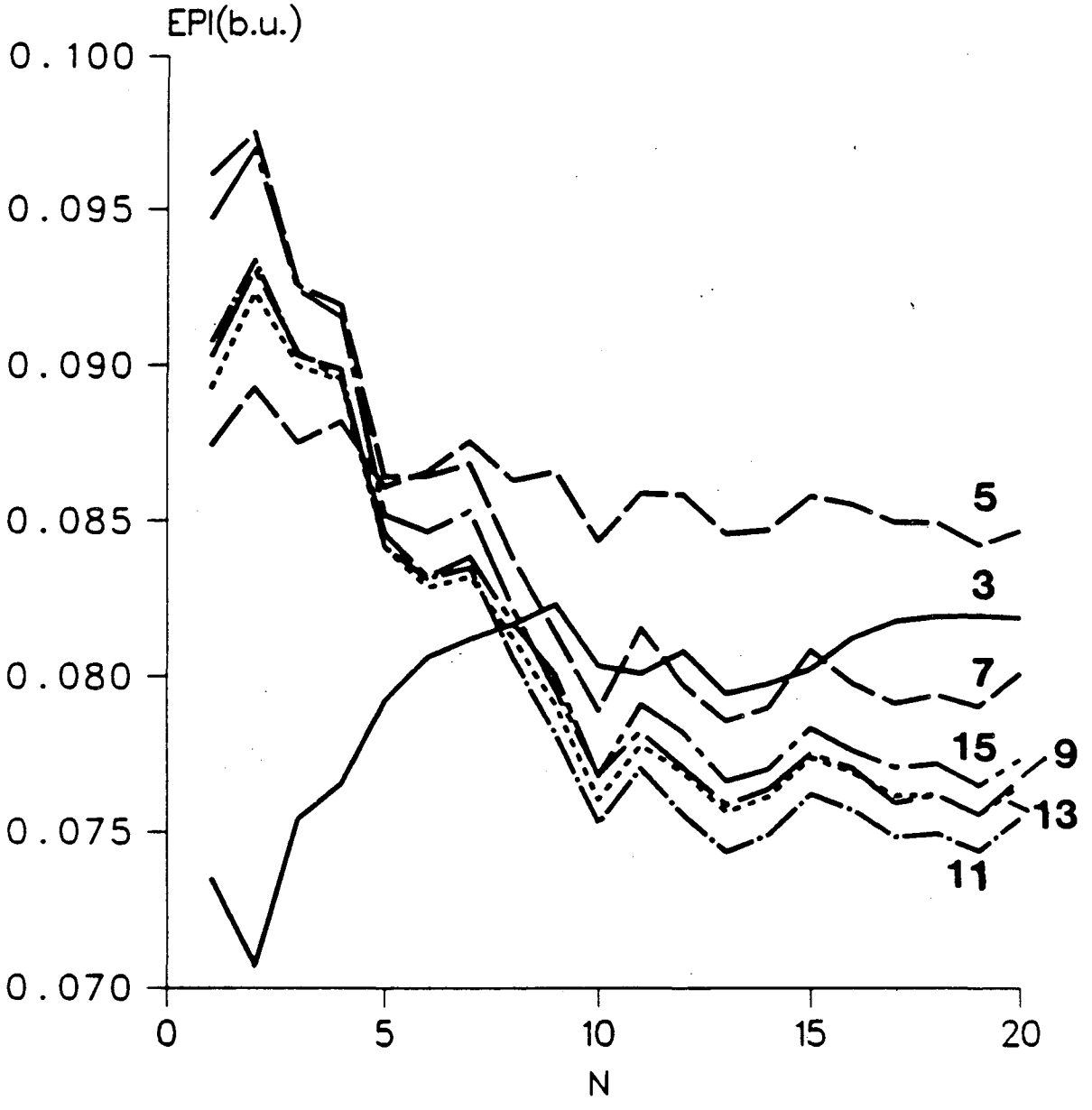

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Fig. 1

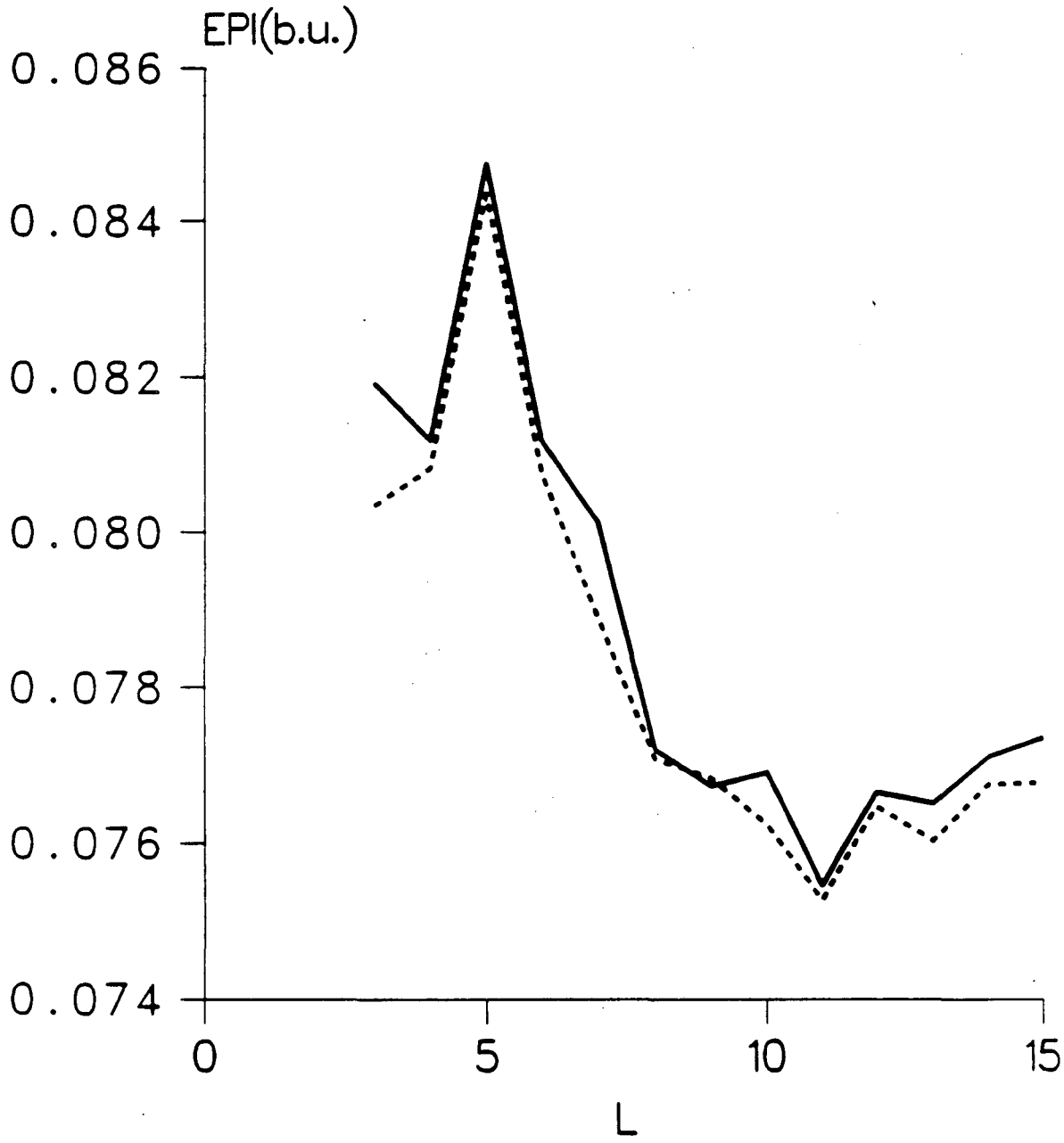

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Fig. 2

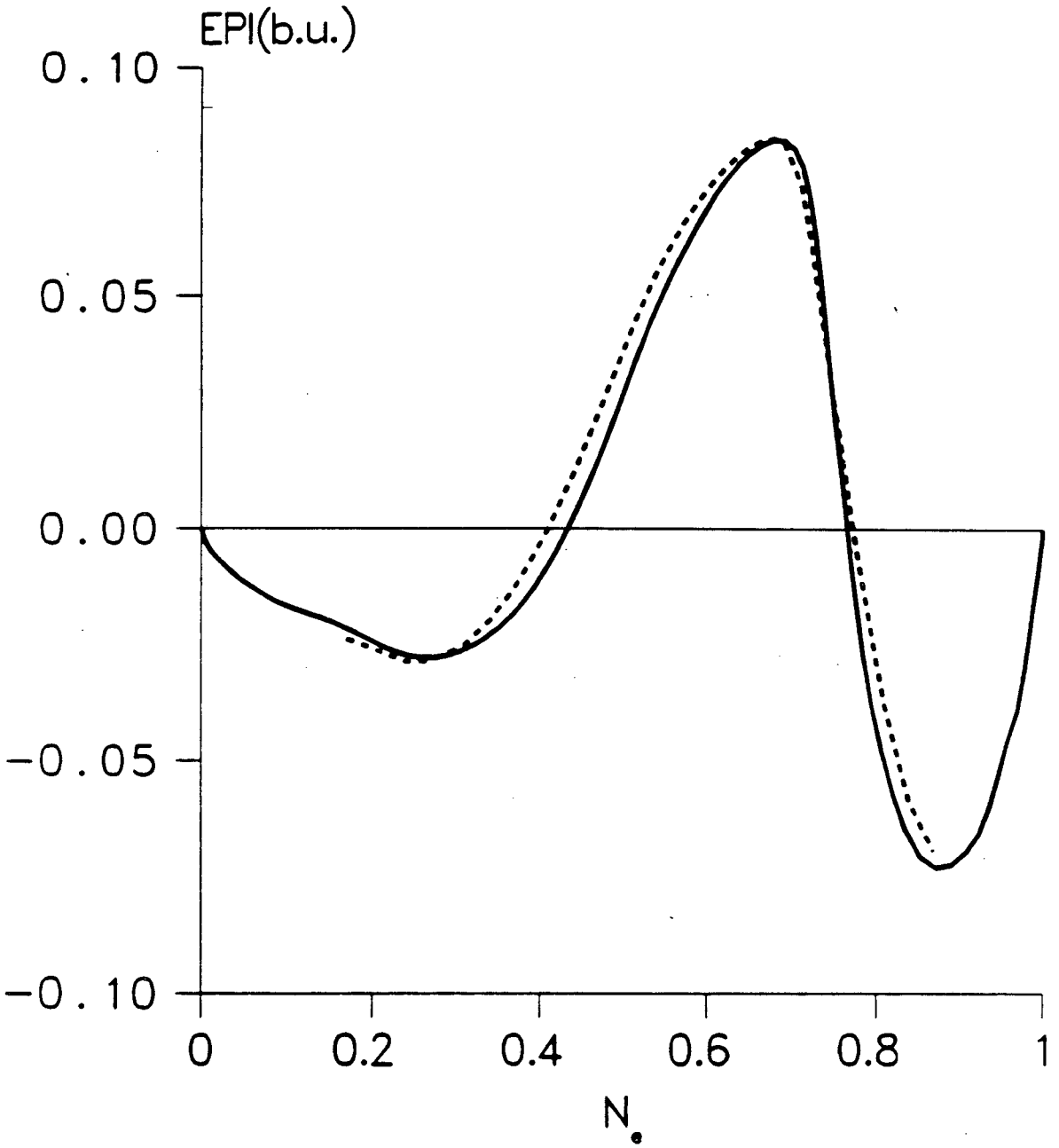

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Fig. 3

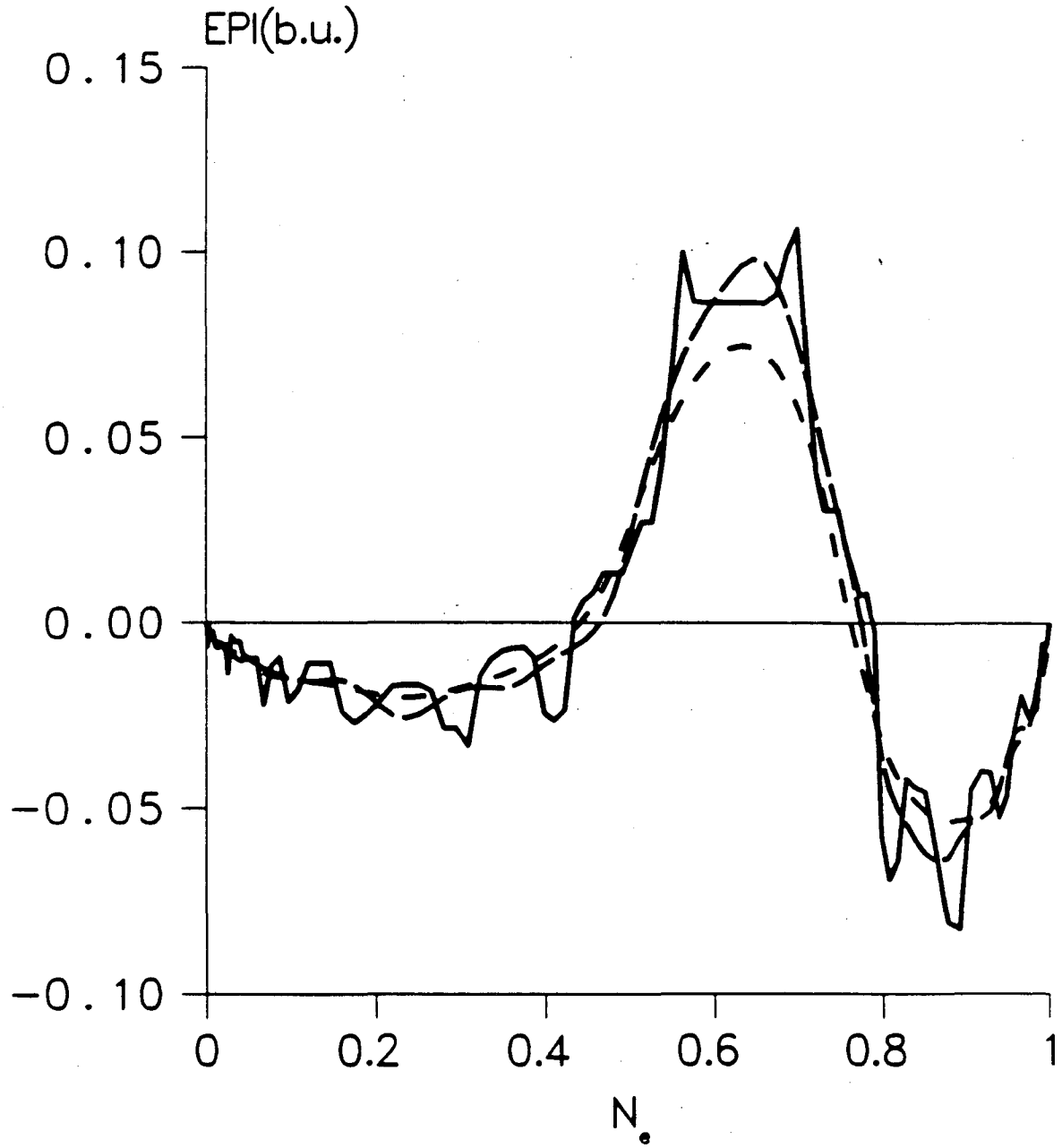

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Fig. 4

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