1. INTRODUCTION

In the last decade, the availability of large parallel computing resources and the development of order N algorithms [1, 2] made feasible ab initio electronic structure calculations in extended metallic systems. A new, surprising, result in the theory of metallic alloys has been obtained by Faulkner, Wang and Stocks, who have analysed density functional theory calculations for unit cells containing hundred to thousand atoms and designed to simulate binary alloys with substitutional disorder. They discovered [3, 4] that the net charge at each crystal site, $q_i$, is related to $V_i$, that part of electrostatic potential at the same site that is due to the interactions with all the other charges in the system, through a simple linear law

$$a_i q_i + V_i = k_i$$

For a specified configuration of the binary alloy $A_{c_A}B_{c_B}$, the coefficients $a_i$ and $k_i$ in Eq. (1) take the values $a_A$ and $k_A$ if the i-th site is occupied by a A atom or $a_B$ and $k_B$ otherwise. Moreover, the sets of coefficients extracted from different samples corresponding to the same mean concentration show up little differences. In the following, these linear relations shall be referred to as the $qV$ laws. The above new findings can be considered empirical in the sense that, although obtained from ab initio calculations, they have not yet been formally derived.

In spite of the simplicity of Eq. (1), for each of the alloying species, the local charge excesses take any value within a certain interval. The corresponding distribution, even for the random alloy model, appears complex and cannot be reproduced, without a proliferation of adjustable parameters, in terms of the number of unlike neighbours of each site [5, 6]. On the other hand, accurate calculations of the alloy total energies and phase equilibria must necessarily keep into account such a distribution. Recently, it has been shown that three coefficients of the $qV$ laws for a binary alloy can be calculated within a single site theory, namely a Coherent Potential Approximation including local fields (CPA+LF) [7]. More precisely, the coefficients $a_A$ and $a_B$ can be viewed as the responses of impurity sites occupied by A or B atoms to local external fields, while the third parameter can be viewed as the difference between the electronegativities of the A and B impurities embedded in the 'mean field alloy' defined by the alloy CPA Green's function.
the local In the present paper, I shall demonstrate that the distribution of charges can be obtained from a variational principle, without any need of sophisticated electronic structure calculations for supercells. For this purpose I shall formulate a Ginzburg-Landau theory in which charge excesses, \( q_i \), play the role of the order parameter field. Hereafter this phenomenological approach is referred to as the 'charge excess functional' (CEF) theory. As it will be seen below, the CEF is completely determined by only three concentration dependent, material specific, parameters. These parameters can be calculated by the CPA+LF theory or extracted from order N calculations. Given the atomic positions within a supercell, the CEF scheme determines the charge excesses at each site, and, hence, the electrostatic energy, with an excellent accuracy. Moreover, the above procedure, using a single set of parameters, can be applied to any ordered, partially ordered or disordered configuration corresponding to the same mean alloy concentration. Furthermore, CEF calculations require really modest computational efforts: 20 seconds CPU time on a 1 GHz Pentium III processor for a 1000 atoms sample. This is a particularly interesting feature as it opens new perspectives. In principle, one could take advantage from these performances and determine, in a parameter free theory, the equilibrium values of the short range order parameter for metallic alloys with an accuracy unprecedented for this kind of calculation. My group is currently developing a new computer simulation technique, based on the joint use of CEF and Metropolis' Monte Carlo that should allow the study of phase equilibria in metallic alloys.

The following of this paper is arranged as follows. In Section II, I shall present the CEF theory and its general solution for the site charge excesses. In Section III, the method will be applied to bcc Cu\(_{0.50}\)Zn\(_{0.50}\) alloys and its accuracy will be tested through a comparison with order N Locally Self-consistent Multiple Scattering (LSMS) theory calculations \([8]\). The comparison will also show that the CEF describes the distribution of charges in metallic alloys with a surprisingly good accuracy, when the material specific parameters are obtained from order N calculations, while fairly good results are obtained using the parameters obtained from the above generalisation of the CPA theory. The final Section IV is devoted to a thorough analysis of the CEF method and of its possible extensions and applications to the study of phase transitions and ordering phenomena in the metallic state.

2. A CHARGE EXCESS FUNCTIONAL FORMALISM FOR CHARGE TRANSFERS IN METALLIC ALLOYS

2.1. THE MODEL

The binary alloy A\(_{c_A}\)B\(_{c_B}\), \( c_A + c_B = 1 \), shall be studied by the means of supercells containing \( N \) 'atoms' with periodic boundary conditions. Each site of the cell can be occupied by a A or a B atom. If the chemical occupations are not considered, the lattice described by the sites within the supercell and their periodic replicas is a simple lattice, with one atom per unit cell. Below, it shall referred to as the 'geometrical lattice'. In order to have a theory flexible enough to deal on equal footing both with ordered and disordered alloys, in principle, one should consider all the \( N! \) different 'alloy configurations' that belong to the statistical ensemble specified by a given molar fraction, \( c_A \). Each configuration is described by the set of 'occupation numbers',

\[
X_i^\alpha = \begin{cases} 
1 & \text{if the } i\text{-th site is occupied by a } \alpha \text{ atom} \\
0 & \text{otherwise} 
\end{cases} 
\]  

(2)

The arrays \( X^A \) and \( X^B \) describe completely an alloy configuration with a certain redundancy, since, for any \( i \), it holds \( X_i^A + X_i^B = 1 \). Below, the convention is used that Latin indices, \( i, j, \ldots \), identify the sites in the supercell, and Greek indices, \( \alpha, \beta, \ldots \), the chemical species, A or B. Moreover, whenever their ranges are not indicated, the sums over the Latin indices run from 1 to \( N \), while the Greek indices take only the values A and B.

A volume \( \omega_i \) is associated with each crystal site. In the following it will be assumed that all the atomic volumes sum up to the supercell volume. There is some arbitrariness in the way in which these volumes can be chosen: they could be built using the Wigner-Seitz construction (and possibly approximated by spheres, as in the case of the Atomic Sphere Approximation),
or they could be non-overlapping muffin-tin spheres to which an appropriate fraction of the interstitial volume is added.

Each site in the supercell is occupied by a nucleus of charge $Z_i$, and, for each site, a charge excess can be defined as follows:

$$q_i = \int_{\omega_i} d\vec{r} \rho(\vec{r}) - Z_i$$

where $\rho(\vec{r})$ is the electronic density. The above charge excesses satisfy a global electroneutrality condition

$$\sum_i q_i = 0$$

Different models for ordered and disordered alloys will be discussed below. The random alloy model can be defined by saying the the occupations of different sites are not statistically correlated, i.e.

$$\langle X_\alpha^i X_\beta^j \rangle = \langle X_\alpha^i \rangle \langle X_\beta^j \rangle$$

or, equivalently, by assuming equal statistical weights for all the alloy configurations in a fixed concentration ensemble. This, evidently, corresponds to the $T \to \infty$ limit for the alloy site occupations. Real alloys, of course, should be studied at finite temperatures and, in order to describe how much they are ordered, it is customary to introduce the short range order parameters [9],

$$p(\vec{r}_{ij}) = \langle X_\alpha^i X_\beta^j \rangle - \langle X_\alpha^i \rangle \langle X_\beta^j \rangle$$

Also a charge correlation function can be defined as

$$g(\vec{r}_{ij}) = \langle q_i q_j \rangle - \langle q_i \rangle \langle q_j \rangle = \langle q_i q_j \rangle$$

Of course, even for random alloys, the excess charges are correlated, i.e. $g(\vec{r}_{ij}) \neq 0$.

2.2. THE CHARGE EXCESS FUNCTIONAL

Within the muffin-tin or the atomic sphere approximation, the electrostatic energy of the system can be written as the sum of site-diagonal terms plus a Madelung term [10, 4]. I shall concentrate on the latter,

$$E_M = \sum_{ij} M_{ij} q_i q_j = \frac{1}{2} \sum_i q_i V_i$$

The Madelung matrix elements $M_{ij}$ in Eq. (8) are defined [11] as

$$M_{ij} = \sum_{\vec{R}} \frac{1}{|\vec{r}_{ij} + \vec{R}|}$$

where $\vec{r}_{ij}$ are the translations from the $i$-th to the $j$-th site within the supercell and $\vec{R}$ are the superlattice translation vectors.

Equation (8) defines also the Madelung potential at the $i$-th site,

$$V_i = 2 \sum_j M_{ij} q_j$$

Everywhere in this paper atomic units are used in which $\epsilon^2 = 2$.

The starting point of the model is the assumption that linear laws hold and relate the charge excess at the $i$-th site $q_i$, and the Madelung potential at the same site $V_i$. As discussed above, this is an evidence from basically exact order N calculations, although also the single site CPA+LF model [7] is able to provide a realistic estimate of the coefficients entering in the linear laws. Therefore, I shall assume that, for some specified configuration, the following equations are satisfied,

$$a_i q_i + 2 \sum_j M_{ij} q_j = a_i b_i = k_i$$

(11)
where \( a_i \) and \( b_i \), the coefficients of the linear laws, are assumed to depend only on the occupation of the \( i \)-th site in the configuration given and then to take the values \( a_A \) and \( b_A \) or \( a_B \) and \( b_B \) depending on the chemical occupation of the \( i \)-th site. Moreover, it is required that the global electroneutrality condition, Eq. (4), must be satisfied.

If all the material specific coefficients, \( a_\alpha \) and \( b_\alpha \), were specified by the mean alloy concentrations, one would have a set of \( N+1 \) equations, Eqs. (11) and (4), and \( N \) unknown quantities to be determined, the \( q_i \). In general, the determinant of this set of equations is not singular and, hence, the problem would be overdetermined. This is not in contrast with the results of order \( N \) calculations: in Refs. [3, 4] it is found that all the four constants are determined for a given configuration, while different configurations corresponding to the same mean alloy concentration are characterised by slightly different sets of constants. Actually, in Ref. [3], the comparison between results for disordered and ordered alloy configurations shows that, for ordered alloys, the constants \( a_\alpha \) have values very close to those found for random alloys at the same mean concentration, while larger discrepancies are found for the constants \( b_\alpha \).

As discussed in Ref. [7], an useful hint for solving the problem comes from the the CPA+LF model. This theory views the quantities \( a_\alpha \) as the responses of the impurity sites, embedded in the CPA ’mean’ alloy, to a local field. Hence, in the CPA+LF model, the same quantities depend only on the mean alloy concentrations. On the other hand, in the same theory, the zero-field charges, \( b_A \) and \( b_B \), are related one to the other through the CPA ’electronegativity’ condition. These facts suggest that, in different configurations corresponding to the same alloy concentration, the constants \( b_\alpha \) are probably renormalised by the global constraint, Eq. (4), while much smaller effects, if any, are expected for \( a_\alpha \).

To make further progresses, consider the following functional of the site charge excesses,

\[
\Omega([q], \mu) = \frac{1}{2} \sum_i a_i (q_i - b_i)^2 + \sum_{ij} M_{ij} q_i q_j - \mu \sum_i q_i
\]  

(12)

where the Lagrange multiplier \( \mu \) has been introduced to impose the global electroneutrality constraint. By functional minimization with respect to the order parameter field \( \{q_i\} \), and to the multiplier \( \mu \), the following set of Euler-Lagrange equations is obtained,

\[
a_i (q_i - b_i) + 2 \sum_j M_{ij} q_j = \mu
\]  

(13)

\[
\sum_i q_i = 0
\]  

(14)

Equation (14) evidently coincides with the electroneutrality condition, Eq. (4). On the other hand, Eq. (13) reduces to Eq. (11) only when \( \mu = 0 \). When \( \mu \neq 0 \), one can think that the renormalization of constants, \( a_i b_i \rightarrow a_i b_i + \mu \) occurs in Eq. (11) in order to ensure the global electroneutrality constraint to be satisfied. If the problem of determining the site charge excesses is redefined as a minimum principle for the Ginzburg-Landau functional \( \Omega \), the four constants \( a_\alpha \), \( b_\alpha \), obtained for a given alloy configuration can be used also for other configurations, since they will be properly renormalised: in other words, the information obtained from a specific configuration is transferable to other configurations belonging to the same fixed concentration ensemble.

The minimum principle for \( \Omega \) leads to a scheme in which the constants \( a_\alpha \), related with the response to the external potential, are not affected by the electroneutrality constraint. Now, since \( \Omega \) has the dimension of an energy and contains the electrostatic energy, \( \sum_{ij} M_{ij} q_i q_j \), one can think that the minimum of the functional

\[
E([q], \mu) = \frac{1}{2} \sum_i a_i (q_i - b_i)^2 + \sum_{ij} M_{ij} q_i q_j
\]  

(15)

corresponds the total electronic energy of the alloy configuration, except but an addictive constant. The quadratic terms in Eq. (15) can be considered as energy contributions associated with local charge rearrangements. Moreover, the quantity \( \mu \), introduced simply as a Lagrange multiplier, can be interpreted as a chemical potential ruling the charge transfers in
metallic alloys. It is evidently related with the usual electronic chemical potential, $\mu_{el}$, that in the ensemble representable version of the density functional theory [12], appropriate for random alloys, enters in the functional through the constraint,

$$\int d\vec{r} \rho(\vec{r}) = \sum_i Z_i$$  \hspace{1cm} (16)

2.3. EXPLICIT DETERMINATION OF THE CHARGE TRANSFERS

In the previous subsection, the functional $\Omega([q], \mu)$, hereafter referred to as the grand potential, has been introduced. Once minimised with respect to its variables, it provides the solution for the charge distribution and the chemical potential in the configuration considered, while the four constants entering in its definition, $a_\alpha$, $b_\alpha$, can be considered as the characteristic parameters for a specific alloy system at some specified concentration. In facts, the constants $b_\alpha$ can be evaluated for any alloy configuration corresponding to the given mean alloy concentration, while the arbitrariety introduced in this way is removed since they will enter in determining the charge distribution only through the combinations $a_A b_A + \mu$ and $a_B b_B + \mu$, as discussed in the previous subsection. Below I shall elaborate the explicit solution of the problem. For this purpose, however, an appropriate formalism is necessary.

Below I shall use a tensor notation and denote the set of all the site charges, $q_i$, simply as $q$. Analogously the sets of the Madelung potentials, $V_i$, and the site occupations, $X_\alpha i$, shall be denoted as $V$ and $X^\alpha$. Thus, e.g., $V = 2M \cdot q$ should be read as $V_i = 2 \sum_j M_{ij} q_j$. Moreover, I introduce the vector

$$f = \sum_\alpha k_\alpha X^\alpha$$  \hspace{1cm} (17)

and the tensor $\Gamma$ with matrix elements

$$\Gamma_{ij} = \sum_\alpha a_\alpha X_\alpha^i \delta_{ij}$$  \hspace{1cm} (18)

where $\delta_{ij}$ is the Kroenecker delta. With this notation, Eqs. (13) and (14) can be rewritten as

$$(\Gamma + 2M) \cdot q = f + \mu(X^A + X^B)$$  \hspace{1cm} (19)

$$(X^A + X^B) \cdot q = 0$$  \hspace{1cm} (20)

Then, the solution for the charge distribution can be written in terms of $\Lambda = (\Gamma + 2M)^{-1}$, as follows

$$q = \Lambda \cdot [(f + \mu(X^A + X^B))] = (k_A + \mu) \Lambda \cdot X^A + (k_B + \mu) \Lambda \cdot X^B$$  \hspace{1cm} (21)

The chemical potential can be determined by multiplying Eq. (21) on the left by $(X^A + X^B)$ and using Eq. (20), e.g.,

$$(k_A + \mu)(\Lambda_{AA} + \Lambda_{BA}) + (k_B + \mu)(\Lambda_{AB} + \Lambda_{BB}) = 0$$  \hspace{1cm} (22)

where, the quantities

$$\Lambda_{\alpha\beta} = X^\alpha \cdot \Lambda \cdot X^\beta$$  \hspace{1cm} (23)

have been introduced. Since the matrices $\Gamma_{ij}$ and $M_{ij}$ are real and symmetric, it follows that also $\Lambda_{ij}$ is real and symmetric and, hence,

$$\Lambda_{\alpha\beta} = \Lambda_{\beta\alpha}$$  \hspace{1cm} (24)

By substitution of Eqs. (22) and (24) in Eq. (21), I find the final result of this section,

$$q = (k_A - k_B) [(1 - y) \Lambda \cdot X^A - y \Lambda \cdot X^B]$$  \hspace{1cm} (25)

where

$$y = \frac{\Lambda_{AA} + \Lambda_{AB}}{\Lambda_{AA} + 2\Lambda_{AB} + \Lambda_{BB}}$$  \hspace{1cm} (26)
TABLE 1. Material specific parameters of the CEF, \(a_{Cu}, a_{Zn}\) and \(k_{Cu} - a_{Zn}\), for a bcc \(Cu_{0.50}Zn_{0.50}\) alloy. The first set of parameters, indicated as LSMS, has been extracted from the \(qV\) data obtained by the 'exact' LSMS calculations in Ref.[8] for a 1024 atoms supercell that simulate a random alloy. The parameters in the second set have been calculated using the CPA+LF model of Ref.[7]. All the quantities are in atomic units.

| LSMS   | CPA+LF   |
|--------|----------|
| \(a_{Cu}\) | 1.84284  | 1.22787  |
| \(a_{Zn}\) | 1.82459  | 1.21890  |
| \(k_{Cu} - k_{Zn}\) | 0.28957  | 0.14035  |

TABLE 2. CEF and CEF-CPA calculations (see the text for explanations) for the same bcc \(Cu_{0.50}Zn_{0.50}\) sample as in Table I are compared with the 'exact' LSMS results of Ref.[8]. \(\langle q \rangle_{Cu}\) and \(\langle V \rangle_{Cu}\) are, respectively, the mean values of the charges and the Madelung potentials at the Cu sites, \(\sigma_{Cu}\) and \(\sigma_{Zn}\) the standard deviations of the charge distributions for Cu and Zn, \(E_{MAD}/N\) is the Madelung energy per atom and 'errors' stand for the mean square deviations between CEF (or CEF-CPA) charges and LSMS charges. All the quantities, unless otherwise stated, are in atomic units.

| CEF    | CEF-CPA | LSMS  |
|--------|---------|-------|
| \(\langle q \rangle_{Cu}\) | 0.099787 | 0.090649 | 0.099783 |
| \(\langle V \rangle_{Cu}\) | -0.038197 | 0.039881 | 0.038188 |
| \(\sigma_{Cu}\) | 0.02507  | 0.03082  | 0.02523  |
| \(\sigma_{Zn}\) | 0.02801  | 0.03412  | 0.02814  |
| \(E_{MAD}/N\) (mRy) | -2.552   | -2.453   | -2.557   |
| 'errors' | 2.7 \(10^{-6}\) | 1.5 \(10^{-4}\) |

Eq. (25) clarifies that, in the general solution of the CEF for the charge distribution, \(b_A\) and \(b_B\) enter only via the difference \(k_A - k_B = a_A b_A - a_B b_B\), while the dependence on the alloy configuration is conveyed by the quantity \(y\).

The formulation of the charge excess functional, Eq. (12), and the solution for the local charges, Eq. (25) are well defined both for ordered and disordered alloys. This has been possible because of the introduction of the chemical potential \(\mu\): due to this, only three of the four constants that characterise the \(qV\) linear laws enter in the final solution, Eq. (25). These three quantities together with \(y\), determined by the actual alloy configuration, are equivalent to the original set of four constants.

In the next Section, the charge excess functional formalism will be applied to \(Cu_{0.50}Zn_{0.50}\) alloys on a geometrical bcc lattice.

3. CHARGE DISTRIBUTIONS IN BCC CuZn ALLOYS

3.1. TESTING THE CEF MODEL

As discussed above, Eqs. (25-26) completely determine the distribution of charge excesses for a given alloy configuration. The three material specific parameters contained in the CEF can be extracted from order N as well as from CPA+LF calculations. In this section I shall compare the charge excesses obtained by the CEF with order N Locally Self-consistent Multiple Scattering (LSMS) theory calculations [8].
I have selected a specific configuration of a supercell containing 1024 atoms and designed to simulate a Cu$_{0.50}$Zn$_{0.50}$ random alloy on a bcc geometrical lattice for which LSMS calculations were available [8]. Unless otherwise stated, the CEF calculations reported in the present paper have been performed on the same configuration. As reported in Table I, two distinct sets for the three CEF parameters (in this case $a_{Cu}$, $a_{Zn}$ and $k_{Cu} - k_{Zn}$) have been used. The parameters in the first set have been extracted from linear fits of the $qV$ data in Ref. [8], those in the second have been calculated by the CPA+LF model, as described in Ref. [7]. Accordingly, two different sets of CEF calculations have been executed that shall be referred below to as: CEF, for the first set, or CEF-CPA, for the second.

The differences between LSMS and CEF calculations are really small, as it is apparent from Table II: 5 parts over $10^5$ for the mean values of the charges and of the Madelung potentials, 2 parts over $10^4$ for the Madelung energies, less than 1 per cent for the widths of the charge distributions. The distributions, reported in Fig. (1), appear very similar. In order to

![Figure 1. Cu (light histogram) and Zn (dark histogram) charge excesses distributions for the bcc Cu$_{0.50}$Zn$_{0.50}$ 1024 atoms sample of Table I. From top to bottom: LSMS results (Ref.[8]), CEF and CEF-CPA calculations. Atomic units are used.](image-url)
have a more precise assessment of the accuracy of the CEF results, I have compared directly the charge excesses at each lattice site. In Fig. (2), the differences $\Delta q_i = q_i^{CEF} - q_i^{LSMS}$ are plotted. The absolute values of the $\Delta q_i$ are always smaller than 0.005 electrons and no correlation is visible between the size of these ‘errors’ and the chemical occupation of the site. Interestingly, the mean square deviation between the two set of charges, reported in Table I, is of the order of $10^{-6}$, i.e. its size is comparable with the numerical errors in LSMS calculations. The main source of the tiny differences found is that all the CEF charges, by construction, lie on the two straight lines corresponding to the $qV$ laws for each of the alloying species, while the same laws hold only approximately for LSMS calculations. Tests about the transferability of the CEF parameters extracted from one sample to the other samples are currently being performed. Preliminary results already available [13] suggest that, when using parameters extracted from one sample, the CEF is able to reproduce the charge distribution in other samples maintaining the above mentioned accuracy, even when CEF parameters extracted from random samples are used in ordered, partially ordered or segregated samples and vice versa. This transferability of the CEF parameters is a very remarkable result: evidently the renormalization of the constants mentioned in the previous section is able to deal with very different samples and, more important, this implies that the CEF theory is generally applicable to metallic alloys, no matters whether they are ordered, disordered or segregated. Furthermore, the accuracy obtained for the Madelung energy demonstrates that the theory is able to describe very carefully the electrostatic contributions to the energetics of ordering phenomena.

The application of the CEF theory using parameters from CPA+LF calculations has a particular interest since the CPA+LF model is not based on a specific alloy configuration and, therefore, does not require expensive calculations on supercells. In this case, as it can be seen in Table I and Figs. (1-2), the agreement with LSMS calculation is still fairly good: the CEF-CPA underestimates the mean charges about 10 per cent and overestimates the widths of the charge distributions about 25 per cent. These errors somehow compensate giving a Madelung energy correct within 4 per cent. The comparison with LSMS for the charges at each sites, as displayed in Fig. (2), shows up small systematic errors with different signs on Cu and Zn sites. The histograms of the charge distributions present a small overlap around $q = 0$, as it is visible in Fig. (1). Also in this case, as above, preliminary tests [13] shows that the parameters obtained from the CPA+LF theory are transferable, in the sense that the size of the discrepancies between CEF-CPA and LSMS results appear independent on the amount of short range order in the alloy configurations considered. To maintain the same performances, even in the cases of ordered or segregated samples, is a very remarkable success for a theory, the CPA, originally proposed for random alloys. To my knowledge, this is the first time that a single site theory, free of adjustable parameters, is able to reproduce the charge distribution in metallic alloys. Better results have been obtained by the Polymorphous CPA (PCPA) [14] that, although based on the CPA theory, at similarity of 'exact' LSMS calculations, uses supercells and, hence, many different site potentials.

An important quantity, that is particularly relevant for its role in the energetics of metallic alloys [6], is the charge correlation function $g(r_{ij})$. In Fig. (3), I plot $g(r_{ij})$, as obtained from LSMS, CEF and CEF-CPA calculations, again for the 1024 atoms Cu$_{0.50}$Zn$_{0.50}$ random alloy sample of Ref. [8]. As it is apparent, the agreement between LSMS and CEF calculations is excellent, and very good also for the CEF-CPA. The test is particularly interesting since non correlated charge models would give $g(r_{ij}) = 0$ for $r_{ij} > 0$. It could be therefore quite surprising to observe that, at least in the case at hand, the correlations are slightly overestimated by the CEF-CPA model.

3.2. CHARGE EXCESSES VERSUS LOCAL ENVIRONMENTS

The importance of local environments in determining the charge transfers in metallic alloys has been highlighted for the first time by Magri et al. [5]. Their model simply assumes the charge excesses to be proportional to the number of unlike nearest neighbours. When the development of order N calculation allowed a deeper investigation of the problem [3, 4], it was readily clear that such a simple model was not able to describe the details of the
Figure 2. Left frame: $\Delta q_i = q_{CEF}^{i} - q_{LSMS}^{i}$; right frame: $\Delta q_i = q_{CEF-CPA}^{i} - q_{LSMS}^{i}$, where $q_{CEF}, q_{CEF-CPA}$ and $q_{LSMS}$ are, respectively, the site charge excesses at the $i$-th site as obtained by CEF, CEF-CPA or LSMS (Ref.[8]) calculations for the bcc Cu$_{0.50}$Zn$_{0.50}$ sample (see Table I). Open circles: Zn sites; triangles: Cu sites. Atomic units are used.

Figure 3. Normalised charge correlation function $\langle \langle q_i q_j \rangle \rangle / \langle \langle q \rangle \rangle^2$ for the 1024 atoms bcc Cu$_{0.50}$Zn$_{0.50}$ random alloy sample (see Table I). Open circles: LSMS calculations (Ref.[8]), crosses: CEF calculations, filled circles: CEF-CPA calculations. In the inset, a detail of the same curve is plotted. The shell identifier, $i$, is reported in abscissa. Lines joint the points.

Charge distributions. Later on, however, Wolverton et al. [6] generalised Magri's model by introducing additional terms proportional to the number of neighbour in outer shells and achieved appreciable improvements especially for fcc lattices.

The computational flexibility of the CEF method and the fact that it seems able to reproduce almost perfectly LSMS results allow to check the basic assumptions of the class of theories to which the models of Refs. [5, 6] belong. For this purpose I have evaluated the charge distributions in 40 Cu$_{0.50}$Zn$_{0.50}$ bcc random alloy samples, each containing 432 atoms. The CEF parameters have been extracted from the LSMS calculations of Ref. [8] (see Table I). The data obtained are analysed in Fig. (4). In the top frame the individual charge excesses...
Figure 4. Top frame: charge excesses, \( q \), vs. the number of unlike nearest neighbours, \( n_1 \), for bcc Cu\textsubscript{0.50}Zn\textsubscript{0.50} random alloys. Middle frame: \( q \) vs. the number of unlike neighbours in the second shell, \( n_2 \), only for the Zn atoms that have 4 unlike neighbours in the first shell. Lower frame: \( q \) vs. the number of unlike neighbours in the third shell, \( n_3 \), only for the Zn atoms that have 4 and 3 unlike neighbours in the first two shells. Open circles and triangles identify, respectively, Zn and Cu sites. The data plotted have been obtained from CEF calculations on 40 random alloy samples each containing 432 atoms on a geometrical bcc lattice. The CEF parameters used are listed in Table I. Atomic units are used.

are plotted vs. the number of nearest neighbours, \( n_1 \). The existence of correlation between the charge excesses, \( q \), both with the site occupation and \( n_1 \), is evident. However, as it is apparent, the excesses of charge for atoms of the same chemical species and the same number of unlike nearest neighbours can take any value in intervals whose typical widths is about 0.05 electrons, moreover intervals corresponding to different values for \( n_1 \) present appreciable overlaps. The same observations have already been made in Ref. [3], the main difference is that I have considered a much larger number of configurations and used sample all corresponding to the same stoichiometry. The conclusion, however remains the same: \( n_1 \) is not sufficient to characterise the distribution of \( q \). In order to check how much the consideration of the number of neighbours in the second or in the third shell, \( n_2 \) and \( n_3 \), can improve, I have selected all the Zn atoms with \( n_1 = 4 \) and plotted their charges vs. \( n_2 \) (Fig. (4), middle frame) and all the Zn site with \( n_1 = 4 \) and with \( n_2 = 3 \), the corresponding charges are plotted in the lower frame of the same Fig. (4). Although the qualitative picture is not changed, it is clear that, if the occupation of the neighbours in the first three shells is known, the uncertainty on the charge is reduced about one order of magnitude with respect to what can be obtained by considering \( n_1 \) only. In any case, trying to improve Magri’s model by including more and more shells and...
more and more adjustable parameters, in my view, appears misleading in that it obscures the simple fact that a single number, the value of the Madelung field, is able to reduce the uncertainty to an amount comparable with numerical errors in order N calculations.

4. DISCUSSION

I like to conclude this paper by making, in a quite sparse order, some comments about several interesting aspects of the CEF model and discussing about possible future applications of the theory.

i) A Coarse graining over the electronic degrees of freedom. The CEF operates a coarse graining over the electronic degrees of freedom, that are reduced to one for each atom, the local excess of charge, without any appreciable loss of accuracy for the total energy. This is a consequence of the fact that, within theories like the CPA+LF [7] or the PCPA [14] any site diagonal property is a unique function of the Madelung potential, $V_i$, and the nuclear charge at the same site, $Z_i$. As noticed in [7] this uniqueness is due to the mathematical simplicity of the CPA projectors and, therefore, probably does not hold for more exact approaches, where some residual dependence on the site nearest neighbours environment is expected for. Nevertheless, the fact that the CPA theory accurately accounts for the spectral properties of metallic alloys [15] and the quantitative agreement with LSMS calculations found in Refs. [7, 14] suggest that the errors introduced by neglecting the nearest neighbours influence are probably not much larger than numerical errors in order N electronic structure calculations. The previous sentences require some clarification: when referring to the nearest neighbours environment, I mean the effects of the environment not already conveyed by $V_i$. The site Madelung potential, in fact, already contains much information about the occupations of near and far sites, each weighted as appropriate. Although the context was very different, I like to recall that a coarse graining over quantum degrees of freedom has precedents in the concepts of chemical valence and, more quantitatively, in that of electronegativity.

ii) The CEF and the local environments. Previous attempts to build theories dealing with charge transfers in metallic alloys, as, for instance the model of Magri et al. [5] or the charge-correlated CPA of Johnson and Pinski [16], have been focused on the number of unlike neighbours of each site. Subsequent extensions [6] included consideration for the occupations of outer shells. The $qV$ linear relations suggest that the convergence of such schemes in the number of shells is slow, being basically related to the $r^{-1}$ decay of the Coulombian interaction. The CEF model is more effective in that it accounts for these long ranged interactions. This notwithstanding, the models of Refs. [5, 6] suggest routes to possible future refinements of the CEF theory: improvements could be obtained, for instance, by including local fields in the charge correlated CPA model of Ref. [16].

iii) Computational performances of the CEF theory. Modern ab initio order N calculation require a number of operations directly proportional to the number of atoms in the supercell, $N$, unfortunately with huge pre-factors. To fix the ideas, consider the case of LSMS calculations: the number of operations required is given by

$$n_{LSMS} \propto n_L^3 n_{LIZ}^3 n_{it} n_{it} N \approx 6 \cdot 10^9 N$$

(27)

where $n_L = (l_{max} + 1)^2$ is the size of the single site scattering matrices, $n_{LIZ}$ the number of atoms in the local interaction zone, $n_E$ and $n_{it}$ the number of points in the energy mesh and the number of iterations that are necessary to solve the Kohn-Sham equation. The above estimate for the pre-factor is quite optimistic and correspond to assuming $l_{max} = 3$, $n_{LIZ} = 24$, $n_E = n_{it} = 10$. The CEF requires $n_{CEF} = N^3$ operations when using conventional linear algebra algorithms. Accordingly, for a typical size of the supercell, $N = 1000$, the CEF is 3 to 4 orders of magnitude faster than LSMS. Of course, order N matrix inversion algorithms can be used for the CEF also, this would give $n_{CEF} = n_{LIZ}^3 N$, i.e. 5 orders of magnitude faster than LSMS, regardless of the size of the supercell.

iv) A CEF-Monte Carlo mixed scheme. The very remarkable speed up in electronic structure calculations that can be obtained using the CEF has a qualitative relevance because it opens unexplored possibilities. The minimum value of the CEF functional for a given alloy configuration, $X$, can be viewed as the total electronic energy corresponding to that
configuration. Therefore, the same minimum value can be regarded as a functional of the alloy configuration, say:

$$\min_{\{q\}} \Omega([q]; X, c) = E_{el}(X; c)$$  \hspace{1cm} (28)$$

If lattice vibrations and deformations are not considered, $X$ is completely equivalent to the whole set of the atomic positions. If the validity of the Born-Oppenheimer approximation and of a classical approximation for the atomic degrees of freedom are assumed, then $E_{el}(X; c)$ can be regarded as a classical Hamiltonian for the alloy in study. Probably the functional dependence of $E_{el}(X; c)$ on the atomic degrees of freedom, $X$, is too much complicated for exact, even though approximate, statistical studies. My group is currently developing a mixed CEF-Monte Carlo scheme in which a Metropolis Monte Carlo algorithm is used to obtain ensemble averages for the classical Hamiltonian $E_{el}(X; c)$. The goal here is being able to determine ab initio, within a non perturbative method, the thermodynamics, the phase equilibria and the atomic correlation functions for metallic alloys. At the same time, taking advantage of the uniqueness of the site properties within CPA based approaches, such a scheme should allow for a careful determination of the electronic properties along the lines of the LSMS-CPA of Ref. [17].

v) Improving the CEF-CPA. In Section III, the distributions of the site charge excesses in a random alloy system have been studied. The validity of the $qV$ laws implies that also the values of the Madelung field, $V$, at different sites can be described by two distributions $d_\alpha(V)$. With respect to these, a random alloy system can be viewed as a charge glass. In fact, the consequences of the $q$ and $V$ polydispersivity on the energetics of random alloys are similar to those of the polydispersivity of the bond lengths in ordinary glasses. It is easy to see that these distribution satisfy the following sum rules:

$$\int_{-\infty}^{\infty} dV \ d_\alpha(V) = 1$$
$$\sum_\alpha c_\alpha \int_{-\infty}^{\infty} dV \ V \ d_\alpha(V) = 0$$ (29)

On the other hand, the standard CPA theory is based on the implicit assumption that

$$d_A(V) = d_B(V) = \delta(V)$$ (30)

i.e., the CPA considers random alloys as charge monodisperse systems. Therefore, the CEF-CPA scheme presents the inconsistency that, while the parameters entering in the CEF are calculated by assuming the distribution in Eq. (30), the output distributions are typical of charge glasses. As it is well known, appreciable improvements over the standard CPA theory can be achieved by assuming the distribution in Eq. (30), the output distributions are typical of charge glasses. As it is well known, appreciable improvements over the standard CPA theory can be achieved by the SIM-CPA [18] or the screened CPA [16] models. Both theories are based on the prescription $d_A(V) = \delta(V - V_A)$, $d_B(V) = \delta(V - V_B)$, where the $V_\alpha$ are chosen in order to mimic the mean effect of the charge correlations, in such a way that the sum rules are obeyed. Although these are still monodisperse theories, displacing the centre of mass of the distributions allows for substantial improvements. The best CPA-based model to date available, the PCPA of Ujfalussy et al. [14] is a truly polydisperse theory in which the $V$ distributions are defined self-consistently by the supercell used. As a theory based on specific supercells, however, the PCPA cannot (at least, without much labour) make predictions on the atomic correlations. We are currently developing an alternative approach that could maintain the advantages of the CEF-Monte Carlo scheme without paying the price of having non consistent charge distributions. The idea is simple: an approximation very similar to the PCPA theory can evaluate the polymorphous model defined by the $V$ distributions obtained as an output of the CEF-Monte Carlo, rather those defined by a specified supercell. In this way a new set of improved coefficients for the CEF can be obtained. Thus, by iterating the above modified PCPA and the CEF-Monte Carlo, until convergence is obtained for the $V$ distributions, one would obtain a completely ab initio non perturbative quantum theory of metallic alloys able to evaluate, at the same time, electronic and atomistic properties.
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