Local Charge Excesses in Metallic Alloys: a Local Field Coherent Potential Approximation Theory

Ezio Bruno¹, Leon Zingales and Antonio Milici

Dipartimento di Fisica and Unità INFM, Università di Messina, Salita Sperone 31, 98166 Messina, Italy
(November 8, 2018)

Electronic structure calculations performed on very large supercells have shown that the local charge excesses in metallic alloys are related through simple linear relations to the local electrostatic field resulting from distribution of charges in the whole crystal. By including local external fields in the isomorphous Coherent Potential Approximation theory, we develop a novel theoretical scheme in which the local charge excesses for random alloys can be obtained as the responses to local external fields. Our model maintains all the computational advantages of an isomorphous theory but allows for full charge relaxation at the impurity sites. Through applications to CuPd and CuZn alloys, we find that, as a general rule, non linear charge rearrangements occur at the impurity site as a consequence of the complex phenomena related with the electronic screening of the external potential. This notwithstanding, we observe that linear relations hold between charge excesses and external potentials, in quantitative agreement with the mentioned supercell calculations, and well beyond the limits of linearity for any other site property.

PACS: 71.23.-k, 71.20.-b

I. INTRODUCTION

For many years the Coherent Potential Approximation (CPA) [2] has been widely used for calculating the electronic properties of random metallic alloys. There are many reasons for such a fortune: as it has been already pointed out, the CPA allows for a very careful determination of spectral properties [3] and Fermi surfaces [4]. However, for the arguments discussed in the present paper, two other aspects of the CPA are particularly amenable: its simple and elegant formulation [5] in terms of the multiple scattering theory [6] and the fact that, since it cleanly defines a homogeneous mean field alloy, it constitutes a natural starting point for perturbative studies of the fluctuations. The last feature has allowed the development of successful methods for the study of phase equilibria [7] and magnetic phenomena [8] in metallic alloys and led to surprisingly accurate calculations of properties connected with typical Fermi liquid effects, such as spin [9] and concentration waves [10].

Since 1990, in spite of all the above successes, the CPA theory, or, better, the way in which it has been first implemented self-consistently within the density functional theory [11], has been criticised because it does not account for the electrostatic energy that, in metallic alloys, arise from charge transfers [12]. Alternative models have been proposed able to cope with this lack [13] and to determine more accurately total energies and mixing enthalpies. Unfortunately, the theories of this new class do not allow for an easy evaluation of spectral properties and are usually much more computationally demanding than the CPA.

In the last ten years several attempts have been made to improve the CPA theory including electrostatic interactions. The starting point of these modified CPA theories is the consideration of the physical mechanism responsible of the screening of impurity charges in metals, this is generally took into account introducing some screening length of the order of the nearest neighbours distance. Such theories, the screened impurity model by Abrikosov et al. [14] or the screened CPA method by Johnson and Pinski [15] or the more recent model by Zahiroudakis et al. [16], are able to achieve considerable improvements over the standard CPA, both for the total energies and the spectral properties [3,17].

In the last few years, the advent of order N electronic structure calculations [18,19], making feasible the study of large supercells containing hundreds of atoms, has led to a very remarkable result concerning the charge transfers in metallic alloys. Namely, Faulkner, Wang and Stocks [20,21] discovered that local charge excesses in random alloys are related by simple linear relations, the 'qV' laws, to the local electrostatic potentials. This new result, although not yet formally derived within the context of the density functional theory, has been confirmed by other order N calculations [3] and, indirectly, by photoemission experiments [22,23] and does not appear compatible with previously proposed models [12,24]. It is interesting to observe that the existence of qV linear relations has been obtained also within a Thomas-Fermi model [25] and, henceforth, does not appear related with the specific form of the density functional used, but, rather, to the achievement of self-consistency in density functional theory calculations along with the solution of the Poisson equation used for the potential reconstruction.

The new results of Refs. [20,21] changed the scenario: the local charge excesses take all the possible values over some range, they can be described by a distribution that cannot be reproduced just by considering the nearest neighbours environment. The standard CPA theory or its modified versions [14–16], cannot describe such a distribution, nor other kind of models [13] can. A possi-
II. CHARGE TRANSFERS IN METALLIC ALLOYS

A. Charge transfers in the CPA theory.

As noticed by Magri et al. [12], the Coherent Potential Approximation [2] does not include the energetic contributions arising from the charge transfers between different sites in metallic alloys [29]. This notwithstanding, sometimes, the information contained in the CPA theory about the same charge transfers, has been helpful for understanding the physical properties of certain systems [30,31]. Below we shall elaborate about the reasons for this apparent paradox.

The CPA theory (we use the multiple scattering theory formalism [5,32]) deals with a random binary alloy $A_{c_A}B_{c_B}$ by solving for $t_C$ the so called CPA equation,

$$c_A G_A(t_A,t_C) + c_B G_B(t_B,t_C) = G_C(t_C) \quad (1)$$

The three Green’s functions in Eq. (1), $G_A(t_A,t_C)$, $G_B(t_B,t_C)$ and $G_C(t_C)$, refer to the three different problems sketched in Fig. 1. In fact, $G_C(t_C)$ is the Green’s function for an infinite crystal whose sites are all occupied by effective scatterers characterised by the single-site scattering matrix $t_C$. On the other hand, $G_{A(B)}(t_{A(B)},t_C)$ is the Green’s function for a single impurity ‘atom’ described by the single-site scattering matrix $t_{A(B)}$ and embedded in an infinite crystal with all the other sites characterised by the single-site scattering matrix $t_C$. While the homogeneous effective crystal, the ‘coherent’ medium of the CPA theory, let us call it C, is electroneutral, the two impurity Green’s functions lead to net charge excesses, $q_A^0$ and $q_B^0$, in the sites occupied by the A and B impurities. On behalf of Eq.(1), these charge excesses satisfy the condition,

$$c_A q_A^0 + c_B q_B^0 = 0 \quad (2)$$

However, in the coherent medium C, there is no charge transfer from one site to the others, thus, Eq.(2) cannot be interpreted as an ordinary electroneutrality condition. This notwithstanding, the excess charges, $q_A^0$ and $q_B^0$, can legitimately be considered as the amount of charge that the impurity site A(B) would attract from the medium C [29], as in the two configurations on the LHS of Fig. 1. We could think that Eq. (2) describes an indirect charge transfer, from A to C and from C to B. Since C is a mean field approximation that accurately accounts for the electronic properties of the alloy considered [3], we could say that the CPA ‘charge transfers’ in Eq.(2) reflect the electronegativity differences between A and B atoms in the random alloy $A_{c_A}B_{c_B}$ and, hence, contain valuable physical information. To put it into other words: in the physics of metallic alloys the mean field metal C plays the same role of reference system that, for molecules, is played by the H atom according to Pauling’s celebrated concept of electronegativity [33]. A further reason of interest for
the CPA 'charge transfers', $q^0_{A(B)}$, is the fact that these, though obtained from an isomorphous model, at similarity of the 'true' charge transfers, show up dependencies on the alloy concentration that cannot be reproduced by trivial models [30].

An additional difficulty in interpreting $q^0_{A(B)}$ as the 'true' charge transfers in a random alloy is that, on a more physical ground, the presence of a net charge on A should induce charges on the effective scatterers C and these, in turn, would affect the charge on A. Of course, as it is implied by its mean field nature, the CPA theory misses these important charge polarisation effects. It is easy to see that, the inclusion of these effects leads necessarily to a picture in which different sites occupied by atoms of the same kind are no longer equivalent because they are affected in different ways by the charge rearrangements. In such a case, the isomorphous approximation is no longer feasible. This circumstance led Ujfalussy et al. [26] to develop a 'polymorphous' coherent potential approximation (PCPA), in which different site potentials are allowed for.

In this work we shall follow an approach alternative yet complementary to that of Ref. [26]. Borrowing the terminology by Ujfalussy et al., we shall include in the isomorphous CPA local perturbation fields and study the response of the charge density to these perturbations.

### B. Charge transfers in 'exact' multiple scattering theory calculations.

In the last few years, Faulkner, Wang and Stocks [20,21] have extensively studied the distribution of charges that results from their Locally Self-consistent Multiple Scattering (LSMS) [18] calculations in binary metallic alloys. LSMS calculations are basically exact, except for the Local Density and muffin-tin approximations used, and deal with large supercells containing 100 to 1000 atoms, designed to simulate substitutional disorder. The principle result of Ref. [20,21] is that, for a given supercell configuration, a simple linear law relates the net site charges, $q_i$, to the Madelung potentials, $V_i$, at the same sites, say,

$$a_iq_i + V_i = k_i$$

For a binary alloy the quantities $a_i$ and $k_i$ take the values $a_A$ and $k_A$ if the i-th site is occupied by a A atom or $a_B$ and $k_B$ if it is occupied by B. The Madelung potentials $V_i$ depend on the charges at all the crystal sites, through the relationship

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

where the factor 2 comes from using atomic units. The Madelung matrix elements, $M_{ij}$, are defined [34] as

$$M_{ij} = \frac{1}{R} \frac{1}{|r_{ij} + R|}$$

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

Very remarkably, no numerically significant deviations from the linearity have been found, at least in the range of the variations of $q_i$ and $V_i$ likely to occur in metallic alloys. This result, as stressed by the same authors [20,21], is of no means obvious and should be understood as a consequence of the complex charge relaxation phenomena that occur, in the calculations, along with the achievement of self-consistency, or, in the physical world, through the mechanism mentioned in the previous subsection. Actually, it has been shown that simple models assuming the site charges proportional to the number of unlike neighbours [12] lead to site charges distributions [24] not compatible with Eq. (3).

Although the above mentioned $qV$ linear laws have been extracted from first principle calculations, their formal derivation within the density functional theory has not yet been obtained. Therefore, Eq. (3) should be considered as an empirical law that holds, at least, within the basic approximation underlying the LSMS theory, i.e. the local density approximation for the density functional theory and the muffin-tin approximation for the crystal potential. On the experimental side, the validity of Eq. (3) is supported by photoemission spectroscopy measurements on random alloys [22,23].

An aspect of the above phenomenology, crucial for our present concerns, is the fact that, for random alloys, the four constants in Eq. (3) depend only on the site occupations and the supercell configuration [35]. Moreover the same constants exhibit only minor variations for different configurations corresponding to the same mean alloy concentration. Remarkably, the dependence of the above constants on the molar fractions does not appear easy to describe within simple models. All the above circumstances suggest us that the constants in Eq. (3), that appear to depend mainly on the site chemical occupation, could probably be calculated within a isomorphous theory based on the CPA. Below we shall develop such an approach.

### III. RESPONSE TO LOCAL FIELDS OF THE 'CPA ALLOY'.

#### A. The local field CPA (CPA+LF) model

As discussed in the previous section, LSMS calculations suggest that the charge excess at the i-th site of a metallic alloy is determined, at least within the accuracy permitted by numerical errors, by the local Madelung field, $V_i$, and by the site occupation, say A or B, for a given alloy concentration. Borrowing the language of the
Ginzburg-Landau theory, we can think of the whole set of local charges, \( q_i \), as the order parameter field. The phenomenology suggests a local view in which the local excess of charge, \( q_i \), can be considered as the response to the local perturbation field, \( V_i \).

In this section we develop a simple model for the charge response to such local perturbations. At variance of what happens in real systems, for which the local field at the \( i \)-th site is determined by the charges at all the other sites (see, e.g., Eq. (4)), we shall treat the external field \( \Phi \), as a parameter that can be varied at will. We imagine to have an A impurity atom in a otherwise homogeneous crystal with all the other sites occupied by C scatterers. We suppose that the single site scattering matrix of the CPA medium, \( t_C \), and its Fermi energy, \( E_F \), have been determined by the CPA theory for the binary alloy \( A_{x}B_{1-x} \). The local external field, \( \Phi \), takes a constant value within the impurity site volume and is zero elsewhere. This situation is pictorially represented in Fig. 2. To simplify our discussion we shall solve the problem using the Atomic Sphere Approximation (ASA). However, the following considerations hold for any cellular method, and, with minor modifications, also for the muffin-tin approximation.

We shall refer to the impurity A in the presence of the external field \( \Phi \) as to \( (A, \Phi) \). When \( \Phi = 0 \), the site Green’s function associated with it, \( G_A^\Phi(t_A, t_C) \), reduces to the usual CPA Green’s function, \( G_A(t_A, t_C) \). When \( \Phi \neq 0 \), \( G_A^\Phi(t_A, t_C) \) can be readily obtained using the multiple scattering theory impurity formula [32]:

\[
G_A^\Phi(E, \vec{r}, \vec{r}') = \sum_{L, L'} [Z_L^\Phi(E, \vec{r}) r_{A,LL}^\Phi Z_L^\Phi(E, \vec{r}') - Z_L^\Phi(E, \vec{r}) J_L^\Phi(E, \vec{r}') \delta_{LL'}] \tag{6}
\]

where

\[
t_A^\Phi = D_A^\Phi t_C \left[ 1 + \tau_C \left( (t_A^\Phi)^{-1} - t_C^{-1} \right) \right]^{-1} \tag{7}
\]

In Eqs. (6) and (7), \( E \) is the energy, \( t_C \) and \( \tau_C \) are the CPA single site scattering matrix and scattering-path operator, as determined by an isomorphous CPA calculation, i.e. \( \Phi = 0 \), for the alloy at hand. The single site scattering matrix corresponding to \( (A, \Phi) \), \( t_A^\Phi \), is to be determined from the site potential \( V_A^\Phi(\vec{r}) + \Phi \), \( D_A^\Phi \) is the CPA projector relative to the same site potential, \( Z_L^\Phi(E, \vec{r}) \) and \( J_L^\Phi(E, \vec{r}) \) are two orthogonal solutions of the Schrödinger equation for the same potential, chosen in such a way that the first behaves regularly at \( r = 0 \). In our notation \( L = (l, m) \) labels the angular momentum quantum numbers and, for sake of simplicity, we omit the energy dependence of all the scattering matrices. A complete account of the notation can be found in Refs. [32].

The charge density corresponding to \( (A, \Phi) \) is obtained integrating Eq. (6) over the energy to the Fermi level,

\[
\rho_A^\Phi(\vec{r}) = \frac{1}{\pi} Im \left\{ \int_{-\infty}^{E_F} dE \ G_A^\Phi(E, \vec{r}, \vec{r}' = \vec{r}) \right\} \tag{8}
\]

The corresponding site potential, \( V_A^\Phi(\vec{r}) \), can be reconstructed by solving the appropriate Poisson equation and adding the exchange-correlation contribution [36,37]. Unless \( \Phi = 0 \), it will be different from the site potential obtained from the zero field CPA theory, \( V_A(\vec{r}) = V_A^\Phi=0(\vec{r}) \), due to charge relaxations expected to screen in part the external field. In a numerical implementation of the theory, Eqs. (6-8) and the potential reconstruction need to be iterated starting from a convenient initial guess, until convergence is achieved for \( V_A^\Phi(\vec{r}) \), or equivalently, for \( \rho_A^\Phi(\vec{r}) \). Hereafter we shall refer to the above model as to the Local Field CPA (CPA+LF).

Once convergence is obtained for the charge density, the net charge on the site A can be obtained by integrating over the atomic sphere volume and subtracting the nuclear charge, \( Z_A \),

\[
q_A(\Phi) = \int d\vec{r}\rho_A^\Phi(\vec{r}) - Z_A \tag{9}
\]

It is important to realise that, while the above self-consistent determination of \( V_A^\Phi(\vec{r}) \) or \( \rho_A^\Phi(\vec{r}) \) allows for full charge relaxation at the impurity site, the CPA+LF does not modify the properties of the CPA medium C; these remain specified by the quantities \( t_C \) and \( E_F \) determined at zero external field. In other words, the charge relaxation that is likely to occur also in the neighbouring sites is not accounted for.

Although in this paper we deal only with random alloys, we like to mention that our formalism can be applied also to the study of the screening phenomena in pure systems. In this case, of course, the CPA scattering matrices, \( t_C \) and \( \tau_C \), in Eq. (7) should be replaced by their counterparts for a pure system.

### B. CPA+LF results for CuZn and CuPd alloys: the charge relaxation

We have implemented the CPA+LF theory within our well tested KKR-CPA code [38]. If \( t_C \) and \( \tau_C \) from a previous standard KKR-CPA calculation are stored on a convenient energy mesh, the extra computational efforts required by the CPA+LF calculation are negligible.

In this paper we discuss results for fcc CuPd and for bcc and fcc CuZn random alloys at several concentrations. In all the cases we have used the Local Density approximation (LDA) for the exchange-correlation potential [39], the ASA approximation for the site potentials and the angular momentum expansions have been truncated at \( l_{\text{MAX}} = 3 \). We have a fully relativistic treatment for core electrons and use a scalar relativistic approximation for valence electrons. For all the alloy systems considered in this paper, the lattice parameters have been kept fixed on varying the concentration. In particular, we set \( a = 5.5 \) a.u. and \( a = 6.9 \) a.u. for bcc and fcc CuZn, and \( a = 7.1 \) a.u. for fcc CuPd. The reasons for this choice are, in first place, avoiding the consideration of the lattice parameter variations, not relevant for
the purpose of this paper, and, in second place, allowing for an easier comparison with the results of Refs. [20,21]. For future reference, we mention that with this choice, the atomic volumes in fcc and bcc CuZn alloys differ only about 1.3 per cent.

As we said, the CPA+LF model allows for the determination of the response to an external potential field by the electrons inside the atomic sphere \( \Lambda \). More specifically, the difference

\[
\Delta V_{\alpha}^\Phi(\vec{r}) = V_{\alpha}^\Phi(\vec{r}) + \Phi - V_{\alpha}^{\Phi=0}(\vec{r})
\]

(10)
can be interpreted as the sum of the external field, \( \Phi \), and the internal screening field inside the atomic sphere. Some typical trends for this quantity are shown in Fig. 3. There we report \( \Delta V_{\alpha}^\Phi(\vec{r}) \), \((\alpha = Cu, Pd)\), for an fcc Cu\(_{0.50}\)Pd\(_{0.50}\) random alloy, that we have selected as a typical case. At the Wigner-Seitz radius, \( r_{WS} \approx 2.77 \) a.u., the internal field is able to screen about one half of the external field, both for Cu and Pd impurities, while the screening is almost complete for \( r < 1 \) a.u.. Apparently, the effect of the screening is far from being just a constant shift of the local chemical potential: if that was the case, in Fig. 3 we would have just equally spaced horizontal lines. What we observe is much more complicated. For instance, in the case of Pd impurities we see that, for the largest values of \( \Phi \) considered, \( \Delta V_{\alpha}^\Phi(\vec{r}) \) takes negative values at small \( r \)’s, thus, in the case of Pd, the external field appears overscreened in the same range of \( r \).

The complex nature of the screening phenomena is further confirmed by a look at the electronic densities. In Fig. 4 we plot the excess charge density induced by the external field

\[
\Delta \rho_{\alpha}^\Phi(\vec{r}) = \rho_{\alpha}^\Phi(\vec{r}) - \rho_{\alpha}^{\Phi=0}(\vec{r})
\]

(11)
both for Cu and Pd sites, again for random fcc Cu\(_{0.50}\)Pd\(_{0.50}\). The largest effects come from the large \( r \) region, where the electron density decreases on increasing \( \Phi \) (everywhere in this paper the expressions “electronic density” or ”charge density” are used indifferently with the meaning of ”electron number density”, i.e. the charge factor, \( -e \), is not included). In the innermost part of the atomic spheres, the variations of the charge density sometimes may have opposite sign with respect to that observed close to the cell boundary.

We have considered also the quantity,

\[
b_{\alpha}^\Phi(\vec{r}) = \frac{\rho_{\alpha}^\Phi(\vec{r}) - \rho_{\alpha}^{\Phi=0}(\vec{r})}{\Phi} \approx \frac{\partial}{\partial \Phi} \log \rho_{\alpha}^\Phi(\vec{r})
\]

(12)
that, in the limit \( \Phi \to 0 \) reduces to the logarithmic derivative of \( \rho_{\alpha}^\Phi(\vec{r}) \) and that, on the basis of a formal scattering theory analysis [40] is expected to have a weak dependence on \( \Phi \). As we can see from Fig. 5, the residual dependence on \( \Phi \) is about a few per cent in a relatively small \( r \) interval not far from \( r_{WS} \) and less then 1 per cent in most of the atomic sphere. Although the information conveyed by Fig. 5 can be valuable for the purpose of improving the initial guesses for the charge densities, however the dependence of \( b_{\alpha}^\Phi(\vec{r}) \) on \( r \) appears still quite complicated: \( b_{\alpha}^\Phi(\vec{r}) \) is very small at small \( r \)’s and takes its largest (negative) value at about 2.3 Bohr radii for Cu and 2.4 Bohr radii for Pd. In this region of the atomic sphere the charge density appears most sensitive to the external field.

C. CPA+LF results for CuZn and CuPd alloys: the site charges

As discussed in the previous subsection, the charge relaxation phenomena occurring when the local field \( \Phi \) is included in the isomorphous CPA theory are quite complicated. It is then surprising to see that the corresponding site charges, calculated from Eq. 9, exhibit much simpler trends.

In Fig. 6 we report \( q_{\alpha} \) \((\alpha = Cu, Pd)\) vs. \( \Phi \) for a Cu\(_{0.50}\)Pd\(_{0.50}\) fcc random alloy. As it is evident, the data can be fitted very well by two straight lines, one for each atomic species. The resulting correlations differ from one by less than one part over a million. Interestingly, the slopes of the two lines are different by a relatively small but statistically relevant amount, about 5 per cent. We notice that in Fig. 6 we have considered also \( \Phi \) values considerably larger than those observed in LSMS calculation or likely to occur in real systems, thus our data support the view that the linearity observed has little to do with the size of \( \Phi \).

We have fitted the \( q_{\alpha} \) vs. \( \Phi \) curves at each molar fraction for fcc Cu\(_{1-c}\)Pd\(_{c}\), fcc Cu\(_{1-c}\)Zn\(_{c}\) and bcc Cu\(_{1-c}\)Pd\(_{c}\) random alloys, at a number of alloy concentrations, using the linear relationships

\[
q_{\alpha}(\Phi) = q_{\alpha}^0 - R_\alpha \Phi
\]

(13)
However, at \( \Phi = 0 \), our CPA+LF model satisfies the CPA ‘electronegativity’ condition, Eq. (2). Henceforth, \( q_{\alpha}^0 \) and \( q_B^0 \) are not independent quantities and we have chosen as the parameters of our fit only the three quantities \( R_A, R_B \) and

\[
\Delta = q_A^0/c_B = -q_B^0/c_A = q_A^0 - q_B^0
\]

(14)
The results of these fits are reported in Table I. The deviations from linearity are always comparable with the numerical errors and the fits cannot be improved significantly using different functional forms. The trends found for the fitting parameters vs. the alloy molar fractions are shown in Fig. 7. The dependence on the concentration is appreciable for all the fitting parameters, as expected on the basis of the arguments developed in Section II. Remarkably, the dependences on the alloy system and on the concentration appear at least as much important as that on the atomic species. Thus, for instance, for a
given alloy system and concentration, there are relatively small differences between the values of $R$ corresponding to sites occupied by different atoms. On the other hand, we find much larger variations for $R_{Cu}$ throughout the alloy systems considered. It is interesting to observe that the trends for the slopes, $R_{Cu}$ and $R_{Zn}$, and for $\Delta$ are very similar in both fcc and bcc CuZn alloys. We notice also that $\Delta$, a measure of the electronegativity difference between the alloying species, exhibits, at least for CuPd alloys, non negligible variations vs. the concentration.

In the model of Ref. [12], the same quantity is assumed independent on the concentration. As we see from Table I, the values for $\Delta$ from our theory are systematically 25-35 per cent smaller than those from LSMS calculations. This is, actually, a feature of the standard CPA theory, because the local fields do not enter in the determination of $\Delta$ and it has already been discussed in the literature [31]. This notwithstanding, the CPA is able to catch the qualitative trends of $\Delta$ vs. the concentration for all the systems considered.

The LCPA+LF model gives for $q$ vs. $\Phi$ the same linear functional form as that obtained for $q$ vs. $V$ from LSMS calculations. However, the differences between the two different sets of calculations forbid, at this stage, a direct comparison of the fit coefficients. In fact, as we have already stressed, our CPA+LF model does not account for charge relaxation outside the impurity site volume. By its construction, the CPA medium C is able to screen the impurity charge at $\Phi = 0$, i.e. $q_0^\alpha$. We can think that this amount of charge is screened by the infinite volume of C. The introduction of the local field at the impurity site causes a local excess of charge, $q_\alpha(\Phi) - q_0^\alpha$, with respect to the standard CPA. In order to have global electroneutrality in the CPA+LF theory, we have to introduce, somewhere outside the impurity site, an opposite amount of charge, $q_0^\alpha - q_\alpha(\Phi)$. This can be accomplished following the ideas contained in the screened impurity model (SIM-CPA) by Abrikosov et al. [14] and supposing that the excess (with respect to the standard CPA) charge at the impurity site, $q_\alpha(\Phi) - q_0^\alpha$, is completely screened at some distance, $\rho$, of the order the nearest neighbours distance, $r_1$. Accordingly, each of the $n$ nearest neighbours of the impurity cell shall have, in the mean, a net charge excess $(q_0^\alpha - q_\alpha(\Phi))/n$. This, in turn, will cause an extra field $\Phi_1 = n(2/\rho)(q_0^\alpha - q_\alpha(\Phi))/n = 2(q_0^\alpha - q_\alpha(\Phi))/\rho$ on the impurity site. The total field at the impurity site will be then the sum of the external field $\Phi$ and of the above extra term, in formulae,

$$V_\alpha = \Phi + 2(q_0^\alpha - q_\alpha(\Phi))/\rho \quad (15)$$

Then, by solving for $\Phi$ the last equation and substituting in Eq. (13), we find

$$q_\alpha(\Phi) = q_0^\alpha - \frac{R_\alpha}{1 + 2R_\alpha/\rho} V_\alpha = q_0^\alpha - \tilde{R}_\alpha V_\alpha \quad (16)$$

The coefficients $\tilde{R}_\alpha$ can be compared directly with the slopes of the $qV$ relations from LSMS calculations. However, the comparison, reported in Table I, requires a caveat: we have assumed $\rho = r_1$, i.e. a complete screening at the distance of the nearest neighbours. Actually, the screening lengths in metals are of the order of this distance [41], but our estimate is too crude to expect for a very good quantitative agreement with LSMS calculations in which the charge relaxation is allowed at all the length scales. However, the agreement found is quite satisfactory, within 10 per cent, for CuPd alloys, while larger discrepancies are found for CuZn. Again, the trends for $R_\alpha$ vs. the concentration are qualitatively reproduced.

IV. CONCLUSIONS

Using a convenient generalisation of the CPA theory to include a local external potential, we have been able to reproduce the peculiar linear relationship between the local charge excesses and the local Madelung fields, obtained previously from the analysis of LSMS data [20,21]. Our CPA+LF theory has a very simple structure and, as opposite to LSMS, requires modest computational efforts. The comparison of the linear laws coefficients with those from LSMS calculations is quantitatively satisfactory, though there is place for further improvement. In particular, it has been necessary to include some screening length, that we have kept fixed to the nearest neighbours distance, and that constitute the only non $ab\ ini\ tio$ input of our theory [3]. Work is in progress about this point, and we hope to present in the next future a fully $ab\ ini\ tio$ version of the theory. We think that the CPA+LF model catches the basic physical mechanisms that determine the distribution of the charge excesses in metallic alloys and we are currently working on a new version of the theory in which the distribution of local charge excesses and that of the local fields are obtained self-consistently. We are confident that this will allow for an accurate calculation of the electrostatic contribution to the total alloy energy and believe that these new techniques can prove useful for the study of the phase equilibria in metallic alloys.

The main result of the present paper, having obtained the correct functional form for the $qV$ relations within a CPA-based theory, does not solve the problem of their derivation within the density functional theory. Nevertheless, our work offers a much more comfortable mathematical ground for the search of such a solution and clarifies two points that we like to list below.

1) A conceptual advantage of our CPA+LF theory is that it is build upon a cleanly defined reference medium, the CPA alloy, that is kept fixed. Having fixed the reference medium, the source of the linear laws can be traced only in the CPA projectors and in the site wavefunctions (see Eqs. (6) and (7)), these, in turn, are determined by the nuclear charge on the impurity site and the coupling potential entering in the corresponding Schrödinger-Kohn-Sham equation: in other words, by the chemical species and the Madelung potential. This ensures that,
for a given alloy, i.e. for some specified alloy Green's function, any site property depends only on the chemical species and the Madelung potentials. This applies also, to some extent, to the more realistic LSMS model in which, having fixed the alloy configuration, fixes the system’s Green’s function. Of course, in the LSMS model the Green’s function is determined self-consistently, while in the CPA+LF model we use a reasonable approximation of it: this difference, however, is not essential since in both cases there is a unique Green’s function. A more important difference between CPA+LF and LSMS calculation is the fact that, in the first theory, the way the impurity site is embedded in the system is determined simply by the CPA projectors, while in a more complete treatment of the multiple scattering, as in the case of LSMS calculations, the relationships between the site-diagonal part of the Green’s function at the impurity site and the full system’s Green’s function are more complicated. Also in the last case one could try to define something analogous to the CPA projectors, such generalised projectors, however will depend not only on the systems Green’s function and on the impurity site properties but also on the environment of the neighbouring sites. The fact that the $qV$ laws have been obtained first from the analysis of LSMS data suggests that corrections for the neighbouring sites are really important only for the electrostatic coupling term. This view is supported also by the very remarkable accuracy achieved by the polymorphous CPA theory [26].

ii) Provided that the effect of the nearest neighbours is negligible, on the basis of the above point i), any site property is a unique function of the local field and chemical occupation. This, together with the linear response theory, of course, implies linear $qV$ relations for small fields. However, the range of fields investigated in this paper has been sufficiently wide to encounter non linear behaviours for many quantities, as, for instance, the value of the charge density at some specified $r$. Although the reasons for this remain elusive, we can conclude that the trends for $q$ remain linear beyond the linear response regime for $\rho(\vec{r})$.

After the submission of the present work, two papers [42,43] appeared that treat some of the questions addressed here from a different point of view. In Ref. [42] it is demonstrated that linear $qV$ laws can be obtained within the SIM-CPA model of Abrikosov et al. [14] on varying the effective screening length contained in the same model. Since the SIM-CPA assumes an effective field proportional to the charge excess, and the proportionality constant is the inverse of the above effective length, it is clear that the procedure described in Ref. [42] has effects similar to varying a local external field. Though we believe that the results of Refs. [42,43] offer an independent confirmation of ours, there are important differences between the two approaches. To mention but one: just because of its mathematical construction, the SIM-CPA model forces the $qV$ laws to have the same slopes for both the alloying species, while the LSMS calculations of Ref. [20,21], in agreement with the CPA+LF calculations presented in this paper, find different slopes for different alloying species.

ACKNOWLEDGMENTS

We thank Professor J.S. Faulkner and Dr. Y. Wang for having made available in digital form the data of Refs. [20,21]. We acknowledge also discussions with Professor E.S. Giuliano.

[1] E-mail: bruno@dsme01.unime.it.
[2] P. Soven, Phys. Rev. 156, 809 (1967).
[3] I.A. Abrikosov and B. Johansson, Phys. Rev. B 57, 14164 (1998).
[4] E. Bruno, B. Ginatempo, E.S. Giuliano, A.V. Ruban and Yu. Kh. Vekilov, Phys. Rep. 249, 3353 (1994).
[5] B.L. Gyorffy, Phys. Rev. B 5, 2382 (1972).
[6] J. Korrinda, Physica (Amsterdam) 13, 392 (1947); W. Kohn and N. Rostokler, Phys. Rev. 94, 111 (1954).
[7] B.L. Gyorffy and G.M. Stocks, Phys. Rev. Lett. 50, 374 (1983); J.B. Staunton, D.D. Johnson and F.J. Pinski, Phys. Rev. B 50, 1450 (1994).
[8] J.B. Staunton, F.J. Pinski and D.D. Johnson, J. Appl. Phys. 61, 3715 (1987); J.B. Staunton, J. Poulter, B. Ginatempo, E. Bruno and D.D. Johnson, Phys. Rev. Lett. 82, 3340 (1999).
[9] S.S.A. Razee, J.B. Staunton, B. Ginatempo, F.J. Pinski and E. Bruno, Phys. Rev. Lett. 82, 5369 (1999).
[10] I. Wilkinson, R.J. Hughes, Zs. Major, S.B. Dugdale, M.A. Alam, E. Bruno, B. Ginatempo and E.S. Giuliano, Phys. Rev. Lett. 87, 216401 (2001).
[11] H. Winter and G.M. Stocks, Phys. Rev. B 27, 882 (1983); D.D. Johnson, D.M. Nicholson, F.J. Pinski, B.L. Gyorffy and G.M. Stocks, Phys. Rev. Lett. 56, 2088 (1986).
[12] R. Magri, S.H. Wei and A. Zunger, Phys. Rev. B 42, 11388 (1990).
[13] J.W.D. Connolly and A.R. Williams, Phys. Rev. B 27, 5169 (1983); A. Zunger, S.-H. Wei, L.G. Ferreira and J.E. Bernard, Phys. Rev. Lett. 65, 353 (1990).
[14] I.A. Abrikosov, Yu. Kh. Vekilov and A.V. Ruban, Phys. Lett. A 154, 407 (1991); I.A. Abrikosov, Yu. Kh. Vekilov, P.A. Korzhavhyyi, A.V. Ruban and L.E. Shilkrot, Sol. St. Comm. 83, 867 (1992).
[15] D.D. Johnson and F.J. Pinski, Phys. Rev. B 48, 11553 (1993).
[16] D. Zaharioudakis, J.S. Faulkner and A.N. Andriotis, J. Phys. Condens. Matter 10, 1813 (2000).
[17] J.S. Faulkner, N.Y. Moghadam, Y. Wang and G.M. Stocks, Phys. Rev. B 57, 7653 (1998).
[18] Y. Wang, G.M. Stocks, W.A. Shelton, D.M.C. Nicholson, Z. Sztok and W.M. Temmerman, Phys. Rev. Lett. 75, 2867 (1995).
[19] I.A. Abrikosov, A.M.N. Niklasson, S.I. Simak, B. Johansson, A.V. Ruban and H.L. Skriver, Phys. Rev. Lett. 76, 4203 (1996).
[20] J.S. Faulkner, Y. Wang and G.M. Stocks, Phys. Rev. B 52, 17106 (1995).
[21] J.S. Faulkner, Y. Wang and G.M. Stocks, Phys. Rev. B 55, 7492 (1997).
[22] R.J. Cole, N.J. Brooks and P. Weightman, Phys. Rev. Lett. 78, 3777 (1997).
[23] J.S. Faulkner, Y. Wang and G.M. Stocks, Phys. Rev. Lett. 81, 1905 (1998).
[24] C.Wolverton, A. Zunger, S. Froyen and S.H. Wei, Phys. Rev. B 54, 7843 (1996).
[25] F.J. Pinski, Phys. Rev. B 57, 15140 (1998).
[26] B. Ujfalussy, J.S. Faulkner, N.Y. Moghadam, G.M. Stocks and Y. Wang, Phys. Rev. B 61, 12005 (2000).
[27] In Refs. [42,43] it is argued that the PCPA is equivalent to the Locally Self-consistent Green’s Function method proposed by Abrikosov et al. [19] in the special case in which the local interaction zone is set to contain only one atom.
[28] J.S. Faulkner, Phys. Rev. B 64, 233113 (2001).
[29] The meaning of the world ‘site’ throughout this paper need some clarification. We refer to cellular schemes in which the volumes corresponding to each site sum up to the crystal volume. A different situation occurs in the case of the muffin-tin approximation, because the muffin-tin spheres do not sum up to the crystal volume. Thus, there is no contradiction with the fact that in CPA (as in pure systems) muffin-tin calculations the site-potentials and the total energy contain terms due to the charge transfer from the muffin-tin volumes to the interstitials.
[30] E. Bruno, B. Ginatempo and E.S. Giuliano, Phys. Rev. B 52, 14544 (1995); E. Bruno, B. Ginatempo and E.S. Giuliano, N. Cimento D 20, 1367 (1998).
[31] E. Bruno and B. Ginatempo, Europhys. Lett. 42, 649 (1998).
[32] J.S. Faulkner and G.M. Stocks, Phys. Rev. B 21, 3222 (1980); A. Gonis, Green functions for ordered and disordered systems, North-Holland Elsevier Science Publishers, Amsterdam, The Netherlands (1992).
[33] L. Pauling, The Nature of Chemical Bond, Cornell University Press, Ithaca (1960).
[34] J. M. Ziman, Principles of the theory of solids, Cambridge University Press (1969).
[35] With the expression ”supercell configuration” we always mean the set of the occupations numbers for each site of the supercell.
[36] J.F. Janak, Phys. Rev. B 9, 3985 (1974).
[37] H. Winter and G.M. Stocks, Phys. Rev. B 27, 882 (1983).
[38] E. Bruno and B. Ginatempo, Phys. Rev. B 55, 12946 (1997).
[39] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L.J. Sham, Phys. Rev. 140, A1133 (1965).
[40] E. Bruno, unpublished.
[41] D. Pines, Solid State Phys. 1 (1955).
[42] A.V. Ruban and H.L. Skriver, Phys. Rev. B 66, 024201 (2002).
[43] A.V. Ruban, S.I. Simak, P. A. Korzhavyi and H.L. Skriver, Phys. Rev. B 66, 024202 (2002).
| Alloys       | c   | $\Delta$ | $R_{Cu}$ | $R_X$ | RMS x $10^4$ | $\bar{R}_{Cu}$ | $\bar{R}_X$ | $\Delta$ | $\bar{R}_{Cu}$ | $\bar{R}_X$ |
|--------------|-----|----------|----------|-------|---------------|----------------|-------------|----------|----------------|-------------|
| fcc Cu$_{1-c}$Pd$_c$ | 0.10 | 0.183 | 1.093 | 1.156 | 1.8 | 0.762 | 0.792 | 0.238 | 0.833 | 0.843 |
|              | 0.25 | 0.175 | 1.124 | 1.187 | 2.1 | 0.776 | 0.806 | 0.229 | 0.838 | 0.851 |
|              | 0.50 | 0.160 | 1.184 | 1.244 | 1.9 | 0.805 | 0.832 | 0.219 | 0.843 | 0.851 |
|              | 0.75 | 0.150 | 1.243 | 1.288 | 2.4 | 0.831 | 0.851 | 0.212 | 0.838 | 0.853 |
|              | 0.90 | 0.148 | 1.267 | 1.307 | 4.4 | 0.842 | 0.860 | 0.211 | 0.836 | 0.853 |
| bcc Cu$_{1-c}$Zn$_c$ | 0.10 | 0.109 | 1.206 | 1.232 | 10 | 0.800 | 0.812 | 0.155 | 0.536 | 0.581 |
|              | 0.25 | 0.114 | 1.237 | 1.255 | 10 | 0.814 | 0.822 | 0.159 | 0.526 | 0.554 |
|              | 0.50 | 0.116 | 1.237 | 1.251 | 6.9 | 0.814 | 0.820 | 0.156 | 0.545 | 0.549 |
|              | 0.75 | 0.116 | 1.247 | 1.255 | 5.0 | 0.819 | 0.822 | 0.155 | 0.567 | 0.564 |
|              | 0.90 | 0.116 | 1.248 | 1.254 | 3.2 | 0.819 | 0.822 | 0.158 | 0.582 | 0.577 |
| fcc Cu$_{1-c}$Zn$_c$ | 0.10 | 0.106 | 1.202 | 1.223 | 8.2 | 0.805 | 0.815 | 0.145 | 0.575 | 0.628 |
|              | 0.25 | 0.111 | 1.220 | 1.237 | 8.1 | 0.813 | 0.821 | 0.150 | 0.580 | 0.618 |
|              | 0.50 | 0.116 | 1.222 | 1.241 | 5.5 | 0.814 | 0.822 | 0.151 | 0.600 | 0.622 |
|              | 0.75 | 0.117 | 1.247 | 1.256 | 5.2 | 0.825 | 0.829 | 0.150 | 0.615 | 0.632 |
|              | 0.90 | 0.118 | 1.249 | 1.256 | 3.3 | 0.826 | 0.829 | 0.152 | 0.616 | 0.630 |

TABLE I. Fit parameters for the $q$ vs. $\Phi$ relationships from CPA+LF calculations in fcc Cu$_{1-c}$Pd$_c$, bcc Cu$_{1-c}$Zn$_c$ and fcc Cu$_{1-c}$Zn$_c$ random alloys. The ‘electronegativity difference’, $\Delta$, and the response coefficients, $R_{Cu}$ and $R_X$, ($X = \text{Pd or Zn}$, as convenient) are defined in Eqs. (13) and (15), RMS is the root mean square deviation. The ‘renormalised’ response coefficients, $\bar{R}_{Cu}$ and $\bar{R}_X$, are defined in Eq. (17). On the right we report $\Delta$, $\bar{R}_{Cu}$ and $\bar{R}_X$ from the LSMS calculations of Refs. [19-20].

![FIG. 1. Schematic illustration of the CPA theory. Dark sites are occupied by the CPA coherent scatterer described by the single site scattering matrix $t_C$. The central impurity sites, labelled by A and B, are characterised by the single site matrices $t_A$ and $t_B$.](image1)

![FIG. 2. Schematic illustration of the CPA+LF method. As in Fig. 1, dark sites are occupied by the CPA coherent scatterer described by $t_C$. In the central site, occupied by A, acts also a constant field $\Phi$.](image2)

![FIG. 3. Calculated total field $\Delta V_\alpha(r,\alpha) = \text{Cu, Pd}$ (see Eq. 10) in Cu$_{0.50}$Pd$_{0.50}$ fcc random alloys. The labels indicate the values of the external field, $\Phi$. At the Wigner-Seitz radius, $r_{WS} \approx 2.77$ a.u., the total field results to be about one half of the external field, while the electronic screening is almost complete at $r = 0$.](image3)
FIG. 4. Calculated excess charge density, $4\pi r^2 \Delta \rho_\alpha(r)$ ($\alpha = \text{Cu, Pd}$) (see Eq. 11) in Cu$_{0.50}$Pd$_{0.50}$ fcc random alloys. The labels indicate the values of the external field, $\Phi$.

FIG. 5. The ‘logarithmic derivative’ with respect to the external field (Eq. (12)), $b_\Phi(r)$ ($\alpha = \text{Cu, Pd}$) in Cu$_{0.50}$Pd$_{0.50}$ fcc random alloys. The continuous and the dotted lines refer, respectively, to $\Phi = -0.3$ and $\Phi = 0.3$, i.e. the lowest and the highest $\Phi$ values considered in Fig. 3.

FIG. 6. Site charge excesses $q_\alpha$ ($\alpha = \text{Cu,Pd}$) vs. the external field, $\Phi$, from CPA+LF calculations for Cu$_{0.50}$Pd$_{0.50}$ fcc random alloys. Circles and diamonds, respectively, indicate Cu and Pd impurities.
FIG. 7. Fit coefficients of the linear law $q$ vs. $\Phi$ from CPA+LF calculations for fcc CuPd and fcc and bcc CuZn alloys plotted vs. the Cu content. Upper frame: response coefficients $R_\alpha$, ($\alpha$ refers to the alloying species); lower frame: ‘electronegativity difference’, $\Delta$. The various alloy systems are indicated by labels.
А, Φ