LOCAL CHARGE DISTRIBUTIONS IN METALLIC ALLOYS: A LOCAL FIELD COHERENT POTENTIAL APPROXIMATION THEORY

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1. INTRODUCTION

In the last decade order N electronic structure calculations [1, 2] made possible the study of large supercells containing from 100 to 1000 atoms. Namely Faulkner, Wang and Stocks [2, 3] have shown that simple linear laws, the so called 'qV' relations, link the local charge excesses and the local Madelung potentials in metallic alloys. These qV linear laws have been obtained from the numerical analysis of data produced by Locally Self-consistent Multiple Scattering (LSMS) [1] calculations, while their formal derivation within the density functional theory has not yet been obtained. As a matter of fact, the above laws can be considered to hold at least within the approximations underlying LSMS calculations, i.e. the Local Density and the muffin-tin approximations.

In this paper we shall develop a new version of Coherent Potential Approximation theory (CPA). We apply a local external field and study the response of the mean field CPA alloy. Because of the fluctuation-dissipation theorem, the response to the external field must be equal to the internal field caused by electrostatic interactions. This new theoretical scheme, avoiding the consideration of specific supercells, will enable us to explore a broad range of fields and clarify certain aspects of the mentioned qV relations.

We shall find that, in a quite broad range of applied fields, \( \Phi \), the integrated charge excess at a given site, \( q \), scales linearly with the field, in agreement with the findings of Refs [2, 3]. However, remarkably, in the same range of \( \Phi \) values, the charge density at a given point does not obey a linear scaling. Our results for the CuPd and CuZn alloy systems compare favourably both with the LSMS and conventional superlattice multiple scattering theory calculations, as well as with the available experimental data. Our theory, when applied to random alloys, is computationally inexpensive in comparison with other approaches and can, in principle, be used, in conjunction with statistical methods, to describe ordering phenomena in metallic alloys.

In the next section 2, we shall discuss about charge transfers in multiple scattering theory calculations and CPA theory, while in section 3 we shall describe the above new version of the CPA theory that incorporates local fields (CPA+LF) and apply it to the study of fcc CuPd and fcc and bcc CuZn alloys. In the conclusion we shall summarize the most important features of our work.
2. CHARGE TRANSFERS IN METALLIC ALLOYS.

2.1. CHARGE TRANSFERS FROM LSMS CALCULATIONS.

Faulkner, Wang and Stocks [2, 3] have analysed the distribution of charges in binary metallic alloys as obtained from LSMS calculations. They have studied large supercells with periodic boundary conditions containing hundreds of atoms and designed to simulate substitutional disorder. LSMS calculations are based on the local density approximation to the density functional theory [4, 5] and the muffin-tin approximation for the crystal potential; thus the results of their analysis hold within the same approximations. Below we shall summarize and comment the conclusions obtained in Refs. [2, 3] that are relevant for our present concerns:

i) For a given alloy configuration, the site charges \( q_i \) and the Madelung potentials \( V_i \) obtained from LSMS calculations for binary alloys lie on two straight lines of equations:

\[
a_i q_i + V_i = k_i
\]

where the quantities \( a_i \) and \( k_i \) take the values \( a_A \) and \( k_A \) if the \( i \)-th site is occupied by an A atom and \( a_B \) and \( k_B \) if it is occupied by B. The size of the deviations from linearity appears comparable with the numerical accuracy of LSMS calculations.

The Madelung potentials \( V_i \) entering in Eq. (1) are determined by the charges at all the crystal sites through the relationship:

\[
V_i = 2 \sum_j M_{ij} q_j
\]

where the factor 2 comes from using atomic units. The Madelung matrix elements, \( M_{ij} \), are defined [6] as

\[
M_{ij} = \sum_R \frac{1}{|\vec{r}_{ij} + \vec{R}|}
\]

in terms of the translation vectors from the \( i \)-th to the \( j \)-th site, \( \vec{r}_{ij} \), and the supercell lattice vectors \( \vec{R} \).

ii) For different alloy configurations corresponding to the same molar fractions, the four constants \( a_A, k_A, a_B \) and \( k_B \) in Eq. (1) take different values. This notwithstanding, the variations of the same constants when considering different samples at the same concentration appear much smaller than their variation with the concentration.

iii) The site charge excess corresponding to each chemical species in a random alloy configuration take any possible value in some interval \( q_{\text{min}} \leq q_i \leq q_{\text{max}} \).

Faulkner, Wang and Stocks [2, 3] have stressed that the existence of a linear relation is not a trivial consequence of classical electrostatics. In fact, Eq. (1) is not verified at a generic Kohn-Sham iteration for the charge density in LSMS calculations, while it is found to hold only when convergence is achieved. Thus the linearity of the \( qV \) laws should be interpreted as a consequence of the screening phenomena that occur in metals. As shown by Pinski [7], linear \( qV \) laws can be obtained also by Thomas-Fermi density functional calculations. This circumstance strongly suggests that the linearity of the \( qV \) relations has little to do with the specific form of the density functional used in the calculation. The conclusions drawn in Refs. [2, 3] and summarized above are indirectly supported by photoemission experiments [8, 9]. Moreover, electronic structure calculations based on the Locally Self-consistent Green’s Function method (LSEGF) and the atomic sphere approximation for the crystal potential have also confirmed the linearity of the \( qV \) relations [10, 11, 12].

It should be clear that the definition of charge excess is based on the quite artificial partition of the crystal volume into ”atomic” sites. This partition is accomplished using the muffin-tin approximation in Refs. [2, 3] or the atomic sphere approximation in Refs. [10, 11, 12]. Of course other procedures are possible, but even in the case in which no spherical approximation is made, as it could be for full potential calculations (that unfortunately are not yet available), the way in which the ”atomic cells” are chosen would remain arbitrary. However, different partitions of the crystal volume always lead to linear laws. This has been shown, e.g., in Ref. [11] by changing the ratio \( r \) between the atomic radii associated with each
Figure 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 \( t_B \).

chemical species [13]. To summarize: at least when a spherical approximation is used, the functional form of Eq. (1) is maintained while, of course, the actual values of the coefficients depend on the particular partition used.

As it is evident, the presence of the charge transfers leads to energy corrections that can be important in the physics of metallic alloys. The simple functional form in Eq. (1) allows an easy route for including such corrections [14]. An alternative way for accounting the electrostatic energy contribution due to charge transfers has been proposed by Gonis et al [13, 15]. It consists in choosing the dimensions of the atomic spheres for each alloying species in such a way to have zero charge transfers and, hence, zero contribution to the total energy. Of course, such a procedure could cause large overlap volumes (for simple lattices the overlap volume is minimum when equal atomic spheres are used) and, hence, large errors in density functional theory calculations.

Although, in principle, the quantities \( a_i, k_i \) in Eq. (1) can be influenced by the local environments, it is clear that the consideration of the site chemical occupation only is sufficient to determine the same quantities within an accuracy comparable with the numerical errors in LSMS calculations. This circumstance, as a matter of fact, suggests that a single site theory [16] as the CPA could be sufficient to determine the above \( a_i, k_i \). In section 3 this suggestion shall be analysed.

2.2. CHARGE TRANSFERS IN THE CPA THEORY.

For many years the CPA theory [17] has been used for calculating the electronic properties of random metallic alloys. In fact, the CPA has allowed for very careful studies of spectral properties [10], Fermi surfaces [18], phase equilibria [19] and magnetic phenomena [20] in metallic alloys. Moreover, in spite of its simplicity, the theory has achieved remarkable successes in the calculation of properties related with Fermi liquid effects, such as spin [21] and concentration waves [22]. However, for the purpose of the present work two aspects of the theory are particularly relevant: its elegant formulation in terms of multiple scattering theory [23, 24] and the fact that it constitutes the natural first step for perturbative studies.

As it is well known [25], the CPA does not include the energetic contributions that derive from charge transfers in metallic alloys. In spite of this, the CPA is useful for understanding some physical properties related with these charge transfers. We will try to explain below the reasons for this apparent paradox.

The CPA theory (we shall use the multiple scattering theory formalism [23, 26] for a random binary alloy \( A_{cA}B_{cB} \)) consists of solving for \( t_C \) the so called CPA equation,

\[
c_A G_A(t_A, t_C) + c_B G_B(t_B, t_C) = G_C(t_C)
\]  

The three Green’s functions in Eq. (4), \( G_A(t_A, t_C) \), \( G_B(t_B, t_C) \) 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. (4), these charge excesses satisfy the condition,

\[
c_A q_A^0 + c_B q_B^0 = 0
\]

In C there is no charge transfers from one site to the others and, thus, Eq.(5) cannot be interpreted as an ordinary electroneutrality condition. However \( q_{A(B)}^0 \) can be considered as the charge that the impurity A(B) attracts from the mean medium C, in the sense that there is an indirect charge transfer from A to B, through the mean medium C. The last can be reinterpreted as a reference system and plays a role similar to that of the Hydrogen atom for molecules, in the formulation of the electronegativity theory by Pauling [27].

In summary: we could say that the CPA 'charge transfers' \( q_{A(B)}^0 \) reflect the difference of electronegativity between A and B. Of course the CPA theory, being a single site and a mean field theory, cannot account for the complex charge relaxation phenomena that are expected to make non equivalent sites occupied by same species and surrounded by different local chemical environments. In order to have a picture in which sites occupied by the atoms of the same kind are no longer equivalent, it is necessary to renounce to a single-site picture. Non single-site formulations of the CPA theory have been proposed several times in the literature. Here we mention the charge-correlated CPA by Johnson and Pinski [28] and the Polymorphous Coherent Potential Approximation (PCPA) by Ujfalussy et al [29]. In this paper, we shall develop a different approach by introducing an external local field in a single-site CPA picture; this will allow to maintain all the mathematical simplicity of a single-site theory, nevertheless the presence of external fields will be sufficient to lead to polymorphous site potentials.

3. RESPONSE TO LOCAL FIELDS OF THE ‘CPA ALLOY’.

3.1. THE LOCAL FIELD CPA (CPA+LF) MODEL

In this section, we develop a new version of CPA theory by introducing an external local field \( \Phi \). It will formally enter in the theory as a parameter that can be varied at will. We shall focus on the response of the system due to the resulting rearrangement of the charge distribution.

We imagine 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 \( A_c^0 B_c^0 \). The local external field, \( \Phi \), takes a constant value within the impurity site volume and is zero elsewhere [30]. 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, \( G_A^\Phi(t_D^\Phi, t_C^\Phi) \), reduces to the usual CPA Green’s function, \( G_A(t_A, t_C^\Phi) \). When \( \Phi \neq 0 \), \( G_A^\Phi(t_D^\Phi, t_C^\Phi) \) can be readily obtained using the multiple scattering theory impurity formula [26]:

\[
G_A^\Phi(E, \vec{r}, \vec{r}') = \sum_{L,L'} (Z_{LL'}^\Phi(E, \vec{r}) \tau_{A,LL'}^\Phi Z_{L'L}^\Phi(E, \vec{r}')) - Z_{L,L'}^\Phi(E, \vec{r}) J_{L,L'}^\Phi(E, \vec{r}') \delta_{LL'}
\]

where

\[
\tau_{A}^\Phi = D_{A}^\Phi \tau_C = \left[ 1 + \tau_C \left( (t_D^\Phi)^{-1} - t_C^{-1} \right) \right]^{-1} \tau_C
\]

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 a standard 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, $Z_A^φ(E, \vec{r})$ and $J_A^φ(E, \vec{r})$ are two orthogonal solutions of the Schroedinger equation for the same potential, the first of which is regular 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 Ref. [26].

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

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

(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 [31, 32]. 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 the 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,

$$q_A(\Phi) = \int d\vec{r} \rho_A^\Phi(\vec{r}) - Z_A$$

(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. The resulting lack of self-consistency in the CPA+LF is not a serious drawback if one is interested, as in the present case, to the investigation of trends and general aspects of the screening phenomena.

3.2. CPA+LF RESULTS FOR CUZN AND CUPD ALLOYS: THE SITE CHARGES

We have implemented the CPA+LF theory within our well tested KKR-CPA code [33]. 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 [4], the ASA approximation for the site potentials and the angular momentum expansions have been truncated at $l_{MAX} = 3$. We use a fully
relativistic treatment for core electrons and 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 \(a = 5.5 \text{ a.u.}\) and \(a = 6.9 \text{ a.u.}\) for bcc and fcc CuZn, and \(a = 7.1 \text{ a.u.}\) for fcc CuPd. With this choice, the atomic volumes in fcc and bcc CuZn alloys differ only about 1.3 per cent.

As we shall discuss in the next subsection, the charge relaxation occurring at the impurity site in presence of the external field phenomena are quite complex. Nevertheless, the CPA+LF model gives a simple linear relation between the potential \(\Phi\) and the corresponding site charges. In Fig. 3 we report \(q_\alpha (\alpha = \text{Cu, Zn})\) vs. \(\Phi\) for a Cu\(_{0.50}\)Zn\(_{0.50}\) bcc random alloy. As it is evident, the data can be fitted very well by two straight lines, one for each atomic species (with correlations that 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, slightly less than 2 per cent.

We notice that in Fig. 3 we have considered also \(\Phi\) values considerably larger than those observed in LSMS calculation or likely to occur in real systems; so according to our data the linear relations seem to be valid in a quite broad field range. We have fitted the \(q_\alpha\) vs. \(\Phi\) curves at each molar fraction for fcc Cu\(_c\)Pd\(_1-c\), fcc Cu\(_c\)Zn\(_1-c\) and bcc Cu\(_c\)Pd\(_1-c\) random alloys, at a number of alloy concentrations, using the linear relationships

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

However, at \(\Phi = 0\), our CPA+LF model satisfies the CPA 'electronegativity' condition, Eq. (5), and we have:

\[
c_A q_A^0 + c_B q_B^0 = 0
\]

Henceforth, \(q_A^0\) 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

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

The results of these fits are reported in Table 1. The trends found for the fitting parameters vs. the alloy molar fractions are shown in Fig. 4. The dependence on the concentration is appreciable for all the fitting parameters, as expected on the basis of the arguments in section 2. 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...
TABLE 1. Fit parameters for the $q$ vs. $\Phi$ relationships from CPA+LF calculations in fcc CuPd$_{1-c}$, bcc CuZn$_{1-c}$ and fcc CuZn$_{1-c}$ random alloys [34]. The 'electronegativity difference', $\Delta$, and the response coefficients, $R_{\alpha}$, are defined in Eqs. (10) and (12), RMS is the root mean square deviation. The 'renormalized' response coefficients, $\tilde{R}_\alpha$ are defined in Eq. (14). On the right we report $\Delta$ and $R_{\alpha}$ from the LSMS calculations of Refs. [2, 3].

| Alloys   | $c$  | $\Delta$ | $R_{Cu}$ | $R_{Pd(Zn)}$ | RMS $\times10^4$ | $\tilde{R}_{Cu}$ | $\tilde{R}_{Pd(Zn)}$ | $\Delta$ | $\tilde{R}_{Cu}$ | $\tilde{R}_{Pd(Zn)}$ |
|----------|------|----------|----------|--------------|------------------|------------------|------------------|----------|------------------|------------------|
| fcc CuPd$_{1-c}$ | 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 CuZn$_{1-c}$ | 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 CuZn$_{1-c}$ | 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 |

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. [25], the same quantity is assumed independent on the concentration. As we see from Table 1, the values for $\Delta$ from our theory are systematically smaller than those from LSMS. This fact has not to do with the presence of external fields and it is a feature of the standard CPA theory already discussed in the literature [35]. This notwithstanding, the CPA is able to catch the qualitative trends of $\Delta$ vs. the concentration for all the systems considered. Although the CPA+LF model gives for $q$ vs. $\Phi$ the same linear functional form as that obtained for $q$ vs. $V$ from LSMS calculations, 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 relaxations 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, it is necessary to introduce, somewhere outside the impurity site, an opposite amount of charge, $q^0_\alpha - q_\alpha(\Phi)$. Here it will be accomplished using the arguments of the screened impurity model (SIM-CPA) model by Abrikosov et al. [36]. We suppose 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, $r_1$, of the order the nearest neighbours distance, $r_1$. Accordingly, in the mean, each of the $n$ nearest neighbours of the impurity cell has a net charge excess $(q^0_\alpha - q_\alpha(\Phi))/n$. This, in turn, induces 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 is then the sum of the external field $\Phi$ and of the above extra term, in formulae,

$$V_\alpha = \Phi + 2(q^0_\alpha - q_\alpha(\Phi))/\rho$$ (13)
Figure 4. 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 concen. 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.

Then, by solving for $\Phi$ the last equation and substituting in Eq. (10), we find

$$q_\alpha(\Phi) = q_\alpha^0 - \frac{R_\alpha}{1 + 2R_\alpha/\rho} V_\alpha = q_\alpha^0 - \tilde{R}_\alpha V_\alpha$$  \hspace{1cm} (14)

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 1, 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 [37], 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 $\tilde{R}_\alpha$ vs. the concentration are qualitatively reproduced.

3.3. CPA+LF RESULTS FOR CUZN AND CUPD ALLOYS: THE CHARGE RELAXATION

We have already said, in spite of the $qV$ linear laws, the relaxation phenomena occurring in presence of an external field are complicated. The CPA+LF model allows for the determination of the response to an external potential field by the electrons inside the atomic sphere A.
More specifically, the difference
\[ \Delta V_A^\Phi(\vec{r}) = V_A^\Phi(\vec{r}) + \Phi - V_A^{\Phi=0}(\vec{r}) \] (15)
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. 5. There we report \( \Delta V_\alpha^\Phi(\vec{r}) \), \( (\alpha = Cu, Zn) \), for an bcc \( Cu_{0.50}Zn_{0.50} \) random alloy, that we have selected as a typical case. At the Wigner-Seitz radius, \( r_{WS} \approx 2.71 \) a.u., the internal field is able to screen about one half of the external field, both for Cu and Zn impurities, while the screening is almost complete for about \( r < 1 \) 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. 5 we would have just equally spaced horizontal lines. What we observe is much more complicated. For instance we observe that the screening for small \( r \) is greater in Cu than in Zn. The complex nature of the screening phenomena is further confirmed by a look at the electronic densities. In Fig. 6 we plot the excess charge density induced by the external field
\[ \Delta \rho_A^\Phi(\vec{r}) = \rho_A^\Phi(\vec{r}) - \rho_A^{\Phi=0}(\vec{r}) \] (16)
both for Cu and Zn sites, again for random bcc \( Cu_{0.50}Zn_{0.50} \).

**Figure 5.** Calculated total field \( \Delta V_\alpha^\Phi(\vec{r}) \), \( \alpha = Cu, Zn \) (see Eq. 15) in \( Cu_{0.50}Zn_{0.50} \) bcc random alloys. The labels indicate the values of the external field, \( \Phi \). At the Wigner-Seitz radius, \( r_{WS} \approx 2.71 \) a.u., the total field results to be about one half of the external field, while the electronic screening is almost complete at \( r = 0 \).

**Figure 6.** Calculated excess charge density, \( 4\pi r^2 \Delta \rho_A^\Phi(\vec{r}) \) (\( \alpha = Cu, Zn \)) (see Eq. 16) in \( Cu_{0.50}Zn_{0.50} \) bcc random alloys. The labels indicate the values of the external field, \( \Phi \).
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,

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

(17)

that, in the limit \( \Phi \to 0 \) reduces to the logarithmic derivative of \( \rho_{\Phi}^{\alpha}(r) \) and that, on the basis of a formal scattering theory analysis \([38]\) is expected to have a weak dependence on \( \Phi \). As we can see from Fig. 7, where we plot \( b_{\Phi}^{\Phi}(r) \) for a bcc Cu\(_{0.50}\)Zn\(_{0.50}\) random alloy 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. Moreover this feature appears to be more or less pronounced depending on the system considered, for this reason we plot in Fig. 8 \( b_{\Phi}^{\Phi}(r) \) for a fcc Cu\(_{0.50}\)Pd\(_{0.50}\) random alloy. Although the information contained in Figs. 7 and Fig. 8 can be valuable for the purpose of improving the initial guesses for the charge densities, however the dependence of \( b_{\Phi}^{\Phi}(r) \) on \( r \) appears still quite complicated.

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure7}
\caption{The 'logarithmic derivative' with respect to the external field (Eq. 17), \( b_{\Phi}^{\alpha}(r) \) \((\alpha=\text{Cu,Zn})\) in Cu\(_{0.50}\)Zn\(_{0.50}\) bcc random alloys. The continuous and the dotted lines refer, respectively, to \( \Phi = -0.25 \) and \( \Phi = -0.25 \), the lowest and the highest \( \Phi \) values considered.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure8}
\caption{The 'logarithmic derivative' with respect to the external field (Eq. 17), \( b_{\Phi}^{\alpha}(r) \) \((\alpha=\text{Cu,Pd})\) in Cu\(_{0.50}\)Pd\(_{0.50}\) fcc random alloys. The continuous and the dotted lines refer, respectively, to \( \Phi = -0.25 \) and \( \Phi = 0.25 \).}
\end{figure}
4. CONCLUSIONS

The most important result of this work is the reproduction of the linear laws between local charge excesses and local electrostatic fields, in good quantitative agreement with order N electronic structure calculations [2, 3]. This is very remarkable if one considers the single site nature of our CPA+LF model, that, hence, requires really modest computational efforts. The only non first-principles input of our theory has been the inclusion of a screening length that we have fixed to the nearest neighbours distance. Work is in progress to build a new, completely ab initio, version. The simple mathematical structure of our model has allowed the investigation of a range of fields much broader than that accessible by order N calculations. On this basis, we can conclude that the above linear relations have little to do with the size of the external field. On the other hand, our study shows that, in the same range of fields, non linear trends are clearly observable for other site properties, including the charge density $\rho(r)$ (see, e.g. Figs. 6, 7, 8).

As we have already noticed, the CPA+LF theory fixes the reference medium, the CPA alloy, or, in a more mathematical language, the system Green’s function that depends only on the mean molar fractions. Thus, for a given concentration, any site physical observable depends only on the CPA projectors and the site wavefunctions (see Eqs. (6) and (7)), which, in turn, are completely determined by the nuclear charge on the impurity site and the coupling potential entering in the corresponding Schrödinger-Kohn-Sham equation. Thus, in the CPA+LF theory, any site property is a unique function of the chemical species and of $\Phi$. A question arises: could this uniqueness be maintained in the more realistic multiple scattering theory treatment? We argue that, also in this case, there is a well defined system Green’s function and, in principle ‘site projectors’ $D_i$, could be defined relating the site diagonal part at the site $i$ to the system Green’s function. The excellent performance of the CPA theory about the spectral properties of many alloy systems [10], the present results and those of Ref. [29] suggest that these generalized projectors should be very close to their CPA counterparts, $D_\alpha$, but, in principle, they should also be affected by the chemical environment of the first few neighbours shells of $i$-th site. These effects, if they are important, could be studied, for instance by including local fields in the charge-correlated CPA scheme by Johnson and Pinski [28]. Of course, all the above does not solve the problem of a formal derivation of the $qV$ laws within the density functional scheme, it simply offers a not too difficult mathematical ground in which, we hope, such a derivation could be obtained.

A further advantage of the CPA+LF model is that, in conjunction with the Charge Excess Functional theory [14], it is able to give a good description of the charge distribution in excellent agreement with order N calculations. This, and the flexibility of the scheme, that does not require the use of specific supercells and is then able to deal on the same footing with ordered or disordered configurations, suggest that it constitutes a first step towards an ab initio non perturbative theory of ordering phenomena in metallic alloys.

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