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FIRST-PRINCIPLES LINEAR MUFFIN-TIN ORBITAL ATOMIC-SPHERES APPROXIMATIONS CALCULATIONS IN REAL-SPACE

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"First-Principles Linear Muffin-Tin Orbital Atomic-Spheres Approximations Calculations in Real-Space"

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ABSTRACT

We have developed an approach, based on the LMTO-ASA formalism and the recursion method, which allows us to perform first principles density-functional calculations of electronic structure in real space. Using Zr_2Fe as a test case we compare our results to those obtained by using the standard reciprocal space LMTO-ASA method. The scheme described here can be applied to non-periodic systems and is also very useful in the study of complex metallic systems with a large number of of atoms per unit cell.

To illustrate the application of the first-principle real-space approach to a complex system, we calculate the electronic structure for a cluster of amorphous Zr. We use our results to evaluate the distribution of charge transfer among the sites of this randomly packed system. As a first guess we take the potential parameters to be the same for all atoms. The final self-consistent results show charge transfers which are almost an order of magnitude smaller than the ones obtained in the initial run. The major effect of the self-consistent process in this case is to rearrange the center of the bands, in order to screen large charge fluctuations. This explains why the parametrized LMTO-ASA approach, where the relative position of the bands is fixed using approximate charge neutrality, works so well when applied to transition metal alloys.

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I. INTRODUCTION

With the progress of fabrication and characterization technics, there has been a renewed interest in complex systems, which often lack periodicity. Real space methods such as the recursion method[1] do not require periodicity and their cost when solving an eigenvalue problem grows linearly with the number of non equivalent atoms being considered. Therefore they should be very useful to describe the electronic properties of complex systems, for which the usual k-space methods are inapplicable or extremely costly. Real-space methods are not very practical in general, but they can be extremely efficient when the system in consideration can be well describe by a tight-binding (TB) Hamiltonian. Because localized *d*-bands play a central role in the electronic structure of transition metal alloys, for a long time parametrized TB Hamiltonians and real space methods have been used to understand the behavior of these systems. Usually the parameters are obtained from a LCAO fit to more exact k-space calculations or adjusted to fit experimental results. It is assumed that these parameters can be transferred to describe the more complex systems that one wants to study[2]. The LCAO parametrization has often been extended, with encouraging results, to treat *s* and *p* electrons but the lack of a sound theoretical background to justify the procedure leaves some fundamental questions unanswered. Which are the approximations being used when one forces the Hamiltonian to be tightly bound through a fit? Should the usually extended *s*-*p* electrons be treated within the TB scheme? How do we treat the wave function and quantities which depend on it?

A major progress towards obtaining a tight-binding Hamiltonian

based on a solid theoretical understanding of the problem, came in 1984 with the advent of the LMTO-ASA-TB formalism[3]. The LMTO-ASA is a linear method that treats *s*-*p* and *d* electrons in the same manner. In this formalism, the Hamiltonian can be expressed in terms of different sets of basis functions[3,4]. It can be shown that there is always an appropriate choice of basis set, which generates a tight-binding (TB) Hamiltonian for *s*-*p* and *d* electrons. The sound theoretical framework of the LMTO-ASA formalism allows us to evaluate wave functions, and to know exactly which approximations are being made. Within the LMTO-ASA theory, simple parametrized TB Hamiltonians can be built without the need of fits to more exact calculations or experiment[5]. There are no adjustable parameters in this approach. The parametrized LMTO-ASA-TB scheme is reliable for densely packed systems with small charge transfer between the sites and large values for the local density of states at the Fermi level. It has been used with success to obtain the electronic structure of several ordered and disordered transition metal alloys[5-7]. In the case of semiconductors, magnetic systems, vacancies in metals, surfaces etc.., the parametrized LMTO-ASA TB approach may fail. To obtain reliable results for these systems a more rigorous first-principles, self-consistent density-functional scheme, similar to those implemented in reciprocal space, may be needed. The possibility of using the LMTO-ASA formalism in conjunction with the recursion method in order to perform density-functional calculations in real space was first pointed out by Fujiwara[8]. A more elaborate version of the original approach has been recently published[9]. In both papers the authors are interested in the general properties of amorphous Fe-B alloys. In these calculations they have used for all Fe and B sites the same average Fe

or B potential paramameters, ignoring for the sake of simplicity, local variations of the potential. Within this constraint, the potential parameters for the average Fe and B sites, were made self-consistent. A site by site self-consistency, similar to the ones implemented in reciprocal space, was never attempted.

In this paper we develop a first-principles, self-consistent, LMTO-ASA density functional scheme, which is implemented in real space. The procedure is very similar to the regular k-space LMTO-ASA formalism, but the solution of the eigenvalue problem is done in real space (RS) with the help of the recursion method[1]. This RS-LMTO-ASA approach, in the spin polarized form, was recently used[10] to obtain the electronic structure of ferromagnetic $FeNi_3$ and anti ferromagnetic FeMn. In the present paper we obtain the electronic structure of Zr_2Fe in real-space and compare the results with those obtained using the standard reciprocal space LMTO-ASA formalism. To illustrate the advantages of the real-space approach developed here, we also study the electronic structure of a large randomly packed cluster of amorphous Zr, simulated by a cubic unit cell of 40 non equivalent sites. The distribution of charge transfer between sites at self-consistency, which cannot be obtained via the usual parametrized schemes, is evaluated.

The paper is organized in the following way: In Sec. II, we give a description of the LMTO-ASA and of its several representations. In Sec. III, we describe the real-space self-consistent approach and present some results for Zr_2Fe. In Sec. IV, we discuss the results for the amorphous cluster of Zr and the behavior of the distribution of charge among the Zr sites. Finally, in Sec. V, we present our conclusions.

II. THE LMTO-ASA-TB FORMALISM

The LMTO-ASA formalism is a well known first-principles method and has been described in several papers[3,4,11,12]. A review of the method and its several representations, from a simple real space fixed basis point of view has also been published[8]. A brief description of the method will be given here, to point out which approximations used in the paper and establish the notation. We work in the atomic sphere approximation (ASA), where the space is divided into Wigner-Seitz (WS) cells, which are then approximated by WS spheres of same volume. The LMTO is a linear method and the solutions are most accurate near a freely chosen energy E_ν. Here, as in most of the literature, E_ν is chosen at the center of gravity of the occupied part of the given (s, p or d) band.

The LMTO-ASA basis functions are chosen in order to optimize the efficiency in solving a given problem. To build the basis set we first consider the solutions for an isolated muffin-tin sphere of radius s, with a given spherical potential for $r < s$ and a flat potential outside. It is assumed that the kinetic energy for an electron outside the muffin-tin sphere is approximately zero and the solution of the Schrödinger equation, in this region, reduces to the solution of Laplace's equation. Therefore the non-divergent solution outside the sphere goes as $r^{-\ell-1}$ where ℓ=0,1,2 for s, p and d orbitals, respectively. The solution inside the sphere should match the one outside at the sphere boundary. This set of functions will be used as an envelope in order to force the LMTO-ASA basis set to be continuous and differentiable in all space. The functions $\varphi_\nu(r)$, defined as the radial

part of the solution of the Schrödinger equation for a spherical potential inside each WS sphere at energy E_ν and its energy derivative $\dot{\varphi}_\nu(r)$ defined at energy E_ν, are very fundamental quantities in the LMTO-ASA formalism. They will be used to obtain the LMTO-ASA basis functions, starting from the envelope functions, as described bellow. First we consider the orbital centered at a site **R**. The tail of the envelope function goes as $|r - R|^{-\ell-1}$ outside the central sphere. It is a regular function within every other sphere centered around any R'≠R, and can be expanded around each R' using the regular solutions $|r - R'|^{\ell}$ of the Laplace equation. If we use a scale a and define $r_R \equiv |r - R|$, the tail of the envelope function centered at R can be expressed around any other site R' by the expansion[11]:

$$\left[\frac{r_R}{a}\right]^{-\ell-1} Y_L(\hat{r}_R) = -\sum_{L'} \left[\frac{r_{R'}}{a}\right]^{\ell'} \frac{Y_{L'}(\hat{r}_{R'})}{2(2\ell'+1)} \; S^0_{R'L',RL} \qquad (1)$$

where $L=(\ell,m)$ is a collective angular momentum index and $S^0_{R'L',RL}$ are the well known coefficients of the expansion[11]. The matrix S^0, known as the structure constant matrix, depends on the position of the sites on the given structure, but not on the type of atoms being considered. Now that the envelope function is written in a convenient form, to build the corresponding LMTO-ASA orbital, we substitute the solutions of the envelope inside every WS sphere by a linear combination of $\varphi_\nu(r)$ and $\dot{\varphi}_\nu(r)$, chosen in order to preserve the value of the function and its derivative at the sphere boundary. When built in this way the LMTO-ASA basis is orthogonal to the core levels and provides a much better basis for the actual solutions than the original envelope functions. Using the LMTO-ASA basis set $\{\chi^0_{RL}\}$ we can build the Hamiltonian H^0 and the overlap

matrix O^0 in the usual way. These quantities can be expressed in terms of S^0 and of potential parameters which depend on the values of the functions $\varphi_\nu(r)$ and $\dot{\varphi}_\nu(r)$ at the WS sphere boundary.

Until now we have described the standard LMTO-ASA formalism[12], which does not give rise to a TB Hamiltonian. The structure matrix S^0 entering the Hamiltonian decays as $r^{-2\ell-1}$ with distance and is very long ranged for $s(\ell=0)$ and $p(\ell=1)$ orbitals. Andersen and Jepsen[3] have shown that one of the characteristics of the LMTO-ASA formalism is that that the choice of basis set can be changed to suit ones purpose. A controlled mixing of the original basis set can yield a new basis, built to have a particularly desirable property. For a general basis $\{\chi_{R,L}\}$ the amount of mixing is determined by a set of parameters which depend on ℓ. These parameters define which linear combination of the standard basis, produce the basis set with the desired property. Because the sets are related through mixing, they can be obtained from each other. There are three very important LMTO-ASA representations. The first is the standard representation with no mixing which we have described. The second is the nearly orthogonal representation where the mixing parameters Q_ℓ are chosen to make the overlap matrix close to unity. Finally we have the TB or most localized representation, with a mixing chosen to make the interactions between neighboring sites as short ranged as possible. In the present paper we use a first order TB Hamiltonian where terms of order of $(E-E_\nu)^2$ and higher are neglected. We note that, to this order, the nearly orthogonal and TB representations coincide[4], and we can take advantage of both features. Here, following the literature[4], we use quantities without bars to denote the potential

parameters Q_ℓ, C_ℓ, Δ_ℓ in the nearly orthogonal representation. The mixing Q_ℓ and the other potential parameters C_ℓ and Δ_ℓ in the orthogonal representation are given in terms of the solutions at the boundary of each WS sphere, being different for every non equivalent atom in the system. We will use quantities with a bar ($\bar{Q}_\ell$, $\bar{C}_\ell$ and $\bar{\Delta}_\ell$) to designate quantities in the the most localized (TB) representation. The structure constant matrix $\bar{S}$ for the TB representation, defined by a mixing $\bar{Q}_\ell$ is written in terms of the original canonical structure matrix S^0 of eq.1 as[4]:

$$\bar{S} = S^0(I-\bar{Q}\,S^0)^{-1} \qquad (2)$$

Here I is the unit matrix and $\bar{Q}$ is a diagonal matrix with elements $\bar{Q}_\ell$. The $\bar{Q}_\ell$ that give the TB representation were found empirically[3], by adjusting their values in expression (2), in order to obtain a localized structure constant matrix $\bar{S}$. The values of mixing were found to be approximately independent of the structure[3,4] and are given for *s*, *p* and *d* electrons by $\bar{Q}_s = 0.3485$, $\bar{Q}_p = 0.05303$ and $\bar{Q}_d = 0.010714$.

In the self-consistent real-space approach described in this paper, we will work on the orthogonal representation[11], but will express the orthogonal Hamiltonian in terms of localized parameters of the TB representation. The basis functions of the several representations are not independent, the orthogonal parameters C_ℓ, Δ_ℓ, Q_ℓ are related to the potential parameters $\bar{C}_\ell$ and $\bar{\Delta}_\ell$ of the TB representation. For a given energy E_ν we have[4]:

$$\frac{\bar{C}_\ell - E_{\ell\nu}}{\bar{C}_\ell - E_{\ell\nu}} = \frac{\bar{\Delta}^{1/2}}{\Delta^{1/2}} = 1 - (Q_\ell - \bar{Q}_\ell)\,\frac{C_\ell - E_{\ell\nu}}{\Delta_\ell} \qquad (3)$$

Finally, to first order in $E-E_\nu$ we can express the Hamiltonian H of the orthogonal representation, in terms of TB parameters[3,4] as:

$$H = \bar{C} + \bar{\Delta}^{1/2}\,\bar{S}\,\bar{\Delta}^{1/2} \qquad (4)$$

In the orthogonal representation the overlap matrix is close to unity and we have to solve a simple eigenvalue problem of the form:

$$(H - E)u = 0$$

$$\psi_E = \sum_{RL} \left\{\varphi_\nu(r_R) + (E - E_\nu)\,\dot{\varphi}_\nu(r_R)\right\} Y_L(\hat{r}_R)\; u_{LR}(E) \qquad (5)$$

It is interesting to note that the LMTO-ASA basis functions, when written in this form, can be seen as a Taylor series expansion of an energy dependent partial wave.

III. SELF-CONSISTENT REAL-SPACE SCHEME

Here we present the RS-LMTO-ASA scheme, which allows us to perform first-principles, density functional, electronic structure calculations in real space. As in k-space, the problem in RS can also be divided into two independent parts. First we find the structure constant matrix $\bar{S}$ for the given system. The TB structure constant $\bar{S}$ decreases exponentially with distance and to find the 9x9 matrices connecting each non equivalent site to its neighbours, it is sufficient to invert a cluster of about 20 atoms around the site. Because the values of $\bar{Q}_\ell$ are given by constants, $\bar{S}$ does not change during the self-consistency process. Given $\bar{S}$, to build the Hamiltonian we should find the potential parameters $\bar{C}_\ell$ and $\bar{\Delta}_\ell$. They can be obtained from the orthogonal potential parameters C_ℓ, Δ_ℓ and Q_ℓ using Eq. (3). But to obtain C_ℓ, Δ_ℓ and Q_ℓ we have to solve the Schröedinger equation inside each non-equivalent WS sphere. This part of the problem is often called "the atomic part" and is

treated in the same manner as in the k-space programs. Actually we use regular LMTO-ASA codes when solving for the "atomic part" in the real-space approach. This part gives all the non trivial information about the potential. Therefore the approximations for the exchange and correlation terms which we use in real-space are exactly the same as the ones used in the regular k-space LMTO-ASA formalism. The potential inside a WS sphere and the corresponding potential parameters, are uniquely determined if we give the occupation for each local (s, p and d) band at the site, the first and second moments of the local density of states relative to E_ν and the logarithmic derivative of $\varphi_\nu(r)$ at the sphere boundary[13]. Here (see Table 1) we will use these quantities to compare our results with those obtained in k-space. A brief description of how the potential and potential parameters are obtained from the moments and logarithmic derivatives at the sphere boundary is given below. The spherical average of the charge density inside a WS sphere can be expressed in terms of the radial part of the solutions of the Schröedinger equation inside the sphere, and the moments of the local density of states (LDOS)[4]. To obtain the self-consistent charge density from given moments and logarithmic derivatives in practice, we start from a guessed charge density. The local density potential is made and $\varphi_\nu(r)$ and $\dot{\varphi}_\nu(r)$ are calculated to the given logarithmic derivative. A new charge density is made by occupying the wave functions according to the moments. This procedure is iterated until the atomic sphere is self-consistent. We should note that when we solve for the "atomic part", we choose the potential to be zero at the sphere boundary. When building the Hamiltonian we should correct the relative energy scale of each WS sphere by the electrostatic potential (VES). This correction

includes the Madelung potential due to charged WS spheres of other sites at the given sphere and also take into account, the electrostatic contribution of the sphere itself. Here as in most of the literature, the value of E_ν is chosen in order to keep the first moment of the density of states for the occupied part of the band always zero. To start the self consistent process, we give reasonable guesses for the occupation, second moment and logarithmic derivatives for each non equivalent WS sphere. With this initial conditions, we find the nearly orthogonal potential parameters, use Eq. (3) to obtain $\bar{C}_\ell$ and $\bar{\Delta}_\ell$ and build the real space TB Hamiltonian of Eq. (6). To solve the eigenvalue problem and obtain the LDOS for s-p and d electrons at each non equivalent site, we use the recursion method[1] on a large cluster (of about 1000 atoms) representing the system in question. We then use the LDOS to find the new energy E_ν and the new moments for each band, at each non equivalent site. As in k-space, the new logarithmic derivatives are given in terms of the new values of E_ν and the old values of the potential parameters. We use the new values of the moments and logarithmic derivatives to obtain new values for the orthogonal parameters and new TB parameters $\bar{C}$ and $\bar{\Delta}$. We build a new real space Hamiltonian using expression (5) and the matrix $\bar{S}$. We finally use the recursion method to obtain the local density of states which will be used for the next iteration. The results will be converged when the moments and logarithmic derivatives obtained by solving the eigenvalue problem differ by less than a previously established amount from the ones which have generated the Hamiltonian.

To illustrate the procedure we have obtained the electronic structure of Zr_2Fe. This material forms in a tetragonal structure with

a= 6.385 Å and c= 5.596 Å[14]. It has 12 atoms in the conventional tetragonal cell, but only six atoms in the primitive cell. The LDOS is the same for all Zr atoms and for all Fe atoms. We have performed self-consistent LMTO-ASA calculations in real-space (with the scheme developed here) and in reciprocal space. In reciprocal space we did two calculations: one using for the Hamiltonian the same first order approximation that we have used in real-space and the other using the standard LMTO-ASA approach. In our calculations, the radius of the WS spheres (s_{Fe} = 1.40 Å and s_{Zr} = 1.76 Å) were chosen in order to respect the different sizes of the Zr and Fe atoms.

In our real-space calculations we have used a large cluster of 1372 atoms. To avoid surface effects, the LDOS for a Zr and an Fe atom were obtained via the recursion method, for sites close to the center of the cluster. For both sites, we have used a cutoff parameter LL=20 in the recursion chain[1]. A Beer and Pettifor[15] terminator has been used to obtain the LDOS and its moments. The precision of the results can be increased by using a larger cluster and a larger cutoff parameter LL. But there is always a balance between the precision and the cost. The above values are suitable for our purposes.

We have mentioned that the potential within the sphere is governed by the moments of the local density of states and the logarithmic derivatives. The logarithmic derivative D_ℓ can diverge and to avoid numerical problems we use a related quantity P_ℓ defined by the expression:

$$P_\ell = 0.5 - \mathrm{Artan}\,(D_\ell) / \pi \qquad (6)$$

The quantity P_ℓ is always finite and varies between zero and one.

In this paper we present a new self-consistent approach to

electronic structure calculations, which is implemented in real space. To emphasize the first principles nature of the method, we should demonstrate that, given some fundamental information regarding the system in consideration, the calculations implemented in real-space converge to the expected results. Therefore, when calculating the electronic structure of Zr_2Fe, we took on purpose a very crude initial guess (see Table 1) for the moments and logarithmic derivatives associated with the Zr and Fe sites. The fact that the final results are very close to those obtained using the standard k-space technics shows the reliability of the self-consistent procedure implemented in real-space.

Given the initial guess, we proceeded to use the self-consistent real-space scheme as described above. A mixing of 0.9 of the old values and 0.1 of the new values was used to obtain the potential at each site. Because the step involving the recursion is the most expensive part of the procedure, a rigid band self-consistency was implemented between the iterations, to minimize charge fluctuations due to the large LDOS of the Fe band at the Fermi level and get better parameters for the next iteration. We note that, when applying our criteria for convergence, we compare the moments entering the recursion step with the ones coming out from it.

In table I, we show the converged real-space values (RS), obtained after ten recursion iterations for the Zr and the Fe sites in Zr_2Fe. For comparison, we also show converged k-space results obtained with the same first order Hamiltonian which we use in real-space (FO) and with standard LMTO-ASA calculations (SC). The agreement between real-space and k-space results for the same first order Hamiltonian is excellent,

with occupations differing by less than 2%. We should stress that the real-space results and k-space results were obtained from two completely independent first-principles, density functional calculations. In this context we should note that the recursion method gives the general features of the density of states, but the details can depend on the terminator used. However, the method describes very well integrated quantities and properties which depend on them. Therefore the real space scheme gives only a qualitative description of the density of states at the Fermi level, but is very reliable to obtain magnetic moments electric field gradients at the nuclei, and several other properties. The occupations and moments used in the LMTO-ASA self-consistent scheme are also integrated quantities, and are very well described within the recursion method. Now we should comment on the influence of second order effects. The largest discrepancies between first-order results and those obtained using the full Hamiltonian (SC), are found in the occupations of the s band of Fe. The fact that largest errors are found in the s-band is due to the very wide range of energies spanned by the occupied part of this band. For p and d bands the occupations of RS (or FO) and SC in Table I, agree within 3%. Therefore, if one is interested in properties which do not require a detailed description of the s-band, a first-order Hamiltonian should represent the system well. If a better description of wide bands is needed, two energy windows (more than one E_ν for the same band) could be used. This probably should be done in the case of semi-conductors, where one of the energies E_ν, should be chosen close to the gap.

IV. DISTRIBUTION OF CHARGE TRANSFER IN a-Zr.

To illustrate the application of real space to complex materials, we have used the first-principles RS-LMTO-ASA scheme developed here, to obtain the distribution of charge transfer among the sites in an amorphous Zr (a-Zr) system. The parametrized LMTO-ASA-TB procedure, which works very well in the case of transition metal alloys, imposes approximated charge neutrality around each site and cannot be used to obtain charge transfers. In our calculations, the a-Zr is simulated by a large cluster of about 700 atoms, made of cubic units (a = 9.76 Å) of 40 atoms constructed by random packing of hard spheres (see Table II), relaxed through a Lennard-Jones potential. The Madelung term at each site was calculated for a periodic arrangement of these large cells. In the present calculations, as in the case of Zr_2Fe, we have used in the final steps of convergence, a cutoff parameter LL=20 for the recursion chain and the Beer and Pettifor terminator. In the initial steps of the process a cutoff parameter LL=12 was used.

We have used the exact value for the structure constant matrix $\bar{S}$, obtained from Eq.2 by direct matrix inversion of clusters of about 20 atoms, around each non equivalent site. These quantities are fixed during the self-consistent process. Using Eq.6 and a initial guess for the potential parameters $\bar{C}_\ell$ and $\bar{\Delta}_\ell$, we constructed the Hamiltonian and used the recursion method to obtain the local density of states at each site in the central cube. From the calculated LDOS, we have obtained the charge transfer, the Madelung term and the moments of the LDOS relative to the energy E_ν, taken at the center of gravity of the occupied bands. From this information, taking an appropriate mixing of new and old

moments of the LDOS, we can obtain new potential parameters at each non equivalent Zr site. Usually here one would build the Hamiltonian for the next iteration, use the recursion method to solve the eigenvalue problem and proceed until self-consistency at all sites is achieved. But the recursion step is the heavy part of the calculation and would be good to accelerate convergence by avoiding charge fluctuations between iterations. With this objective in mind, before entering the recursion step, we make the parameters self consistent within the rigid band approximation. This is done by fixing the shape of each s, p and d band, but allowing the centers to be shifted relatively to each other, depending on the values of $\bar{C}_\ell$, obtained at all sites, from the values of the electrostatic potential VES and moments of occupied part of the LDOS. When the potential parameters are converged within the rigid band approach, we proceed to the next recursion step. In all the process we have used a mixing of 0.02 of the new potential into the potential for the previous iteration. Final self-consistency was achieved when the occupations and moments used to obtain the parameters entering the Hamiltonian in a recursion step, differed from those calculated from the resulting LDOS in third decimal place. In the case of occupations for example, we have tolerated differences of a few milli-electrons.

As a initial guess in our calculations we have used, for all the 40 non equivalent sites, potential parameters obtained from regular k-space LMTO-ASA for pure hcp Zr. Therefore the center of the bands in the case of the first guess coincides with that of pure Zr. When the amorphous system is treated self-consistently we find that the Zr band is shifted to higher energies. Here we compare results obtained with parameters of pure Zr and zero electrostatic potential at all sites (initial guess)

with the final self-consistent results for the amorphous cluster. To make the comparisons more meaningful, the energy scales in Fig. 1, Fig. 3a and Fig. 4 are taken relative to the Fermi level. We note that the results obtained with our initial are not the same that we would have obtained using the parametrized LMTO-ASA-TB scheme of Ferreira et al.[5] because here, the approximate charge neutrality around each site has not imposed.

In Fig.1, we show the total density of states for the cluster obtained from the first guess (dotted line) and from the self-consistent results. Because the total DOS is an average among 40 sites, the shape of the band is maintained. If we are not interested in local properties, but only in the general shape of the total DOS, our simple initial guess seems to describe the system well. In this case a self-consistent calculation would not be required.

In Fig.2a, we show the distribution of charge transfer among the 40 sites, resulting from our first guess (empty blocks) and from the converged calculation (dashed blocks). The initial guess gives rather large charge transfers for the system, but in the final results the charge transfer decreases by almost an order of magnitude. We also show (Fig. 2b) the calculated VES at each non-equivalent site. This term is due to the redistribution of charge among the WS spheres and is zero when all spheres are neutral.

In Fig.3, we show, in dashed line, the initial guess used for the parameters $\bar{C}_d$ (Fig. 3a) and $\bar{\Delta}_d$ (Fig. 3b). For comparison we show in the same figures, the final converged distribution of potential parameters $\bar{C}_d$ and $\bar{\Delta}_d$ for the 40 non-equivalent sites. We note that in Fig. 3a the positions of the band centers $\bar{C}_d$ are taken relative to the corresponding

Fermi level. It is clear that the values of $\overline{\Delta}_d$ in all sites are very similar and close to of hcp Zr. The parameters $\overline{C}_d$, relative to the Fermi level, change significantly from site to site around the value obtained for pure hcp Zr. We also note that the effect of the variations of $\overline{C}_d$ at each site, is to screen the excess charge by shifting the center of the band in to appropriate higher or lower energy regions. This variation is mainly due to changes in the electrostatic potential due to charge transfer (see Fig. 2b). This term is the same for all (s, p and d) orbitals at the given site. Therefore, we find a similar behavior for both, $\overline{C}_s$ and $\overline{C}_p$. Comparing Figs. 2a and 3a (or 2b), we see that atoms which had initially too many electrons (site 14, for example) have their bands shifted to higher energies while atoms missing electrons (see site number 6) have their bands shifted to lower energies relative to the average site. This can be seen in Fig. 4 where the initial (dashed lines) and converged (full line) LDOS for sites 6 (Fig.5a) and site 14 are shown. Here again the energy scale was taken with relation to the Fermi level. We see clearly that electrons were expelled from atom 14 and allowed into atom 6 during the self-consistent process in order to reduce the excess charge initially present around these sites. The results of Fig. 4 shows that the LDOS and therefore local properties, are not well described by the Hamiltonian obtained from the potential parameters of pure Zr.

The results show clearly that the main effect of the self-consistent process is to rearrange the potential around each site, in order to screen large charge variations. The potential parameter $\overline{\Delta}_\ell$ is very close to that of the pure metal and the potential parameter $\overline{C}_\ell$ is rearranged in order to screen large charge transfers. This is very

similar to what happens when parametrized LMTO-ASA-TB calculations[5-7] are performed in transition metal alloys. In the parametrized scheme the potential parameters are obtained from pure metals and the relative position of the bands are determined using approximate charge neutrality. In the light of our results it is easy to understand the success of the parametrized approach, when applied to close packed transition metal alloys.

VI. CONCLUSIONS

We have developed a first-principles self-consistent real-space method that can be used to study the electronic structure of complex systems. The method was tested with success in crystalline Zr_2Fe, for which k-space results can be obtained. It was then applied to a non trivial problem; the investigation of the distribution of charge transfer among 40 sites of a random packed structure, simulating amorphous Zr. We find that if the potential parameters of the pure metal is used for all Zr sites in a-Zr, as it was done in our initial guess the charge transfers among the sites are rather large. We show that the effect of self-consistency is mainly to rearrange the potential in order to screen large charge variations. These results support the idea of using approximate charge neutrality to fix the relative position of the bands, used in parametrized calculations in transition metal alloys[5,7]. It also explains why the simple parametrized LMTO-ASA scheme[5], has been used with success, to evaluate subtle quantities such as the behavior of the electric field gradient at the nucleus, for these alloys.

In conclusion, we have presented a new approach to the study of the electronic structure in complex systems. It does not require periodicity

and its cost grows linearly with the number of atoms which have different LDOS. The method is competitive and its potential should be further investigated.

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TABLE I

		ATOM							
		Zr				Fe			
	BAND	GUESS	CONVERGED			GUESS	CONVERGED		
			RS	FO	SC		RS	FO	SC
M0	s	0.600	0.712	0.706	0.671	0.600	0.727	0.719	0.648
	p	0.600	0.726	0.737	0.725	0.600	0.628	0.638	0.658
	d	2.800	2.594	2.588	2.646	6.800	6.581	6.581	6.611
M2	s	0	0.007	0.007	0.006	0	0.006	0.006	0.005
	p	0	0.006	0.006	0.006	0	0.005	0.005	0.005
	d	0	0.015	0.014	0.015	0	0.021	0.021	0.021
P_ℓ	s	0.500	0.640	0.640	0.640	0.500	0.690	0.691	0.698
	p	0.500	0.345	0.344	0.339	0.500	0.440	0.440	0.445
	d	0.500	0.613	0.611	0.608	0.500	0.799	0.802	0.804

Table I. The occupation (M0), the second moment relative to E_ν (M2) and the parameter P_ℓ for the first guess, and converged results. We show converged results obtained in real-space (RS), in k-space with similar first-order Hamiltonian (FO) and in k-space using the standard LMTO-ASA formalism (SC).

TABLE II

ATOM	POSITION (Å)			ATOM	POSITION (Å)		
	x	y	z		x	y	z
01	4.67	3.77	3.95	21	5.23	2.77	6.70
02	7.20	4.67	2.54	22	3.59	5.89	5.91
03	6.80	5.26	6.66	23	6.53	7.17	4.29
04	1.88	3.40	5.89	24	4.95	7.03	8.48
05	5.65	0.81	3.45	25	1.27	7.87	4.69
06	3.73	2.37	1.41	26	3.17	4.24	8.71
07	4.57	5.70	1.45	27	2.08	5.21	3.16
08	3.79	8.02	3.12	28	2.80	0.96	4.36
09	9.31	5.24	4.81	29	4.44	8.77	6.00
10	7.68	2.72	4.81	30	3.05	1.12	7.65
11	8.68	7.65	6.59	31	1.87	8.09	7.66
12	8.46	2.77	7.90	32	3.55	9.19	0.35
13	9.11	7.04	2.33	33	6.45	8.40	1.42
14	7.04	0.32	6.46	34	6.15	3.86	9.49
15	7.92	1.78	1.45	35	0.48	5.32	7.76
16	7.84	6.41	9.35	36	0.53	2.54	3.22
17	1.06	1.86	9.66	37	8.50	9.59	3.84
18	1.81	6.73	0.54	38	9.69	4.38	0.87
19	5.92	0.88	9.13	39	8.92	9.29	9.21
20	0.34	0.73	6.30	40	1.12	9.49	2.02

TABLE II. In this table, we show the positions of the 40 non equivalent atoms in the cubic unit with a = 9.76 Å, used in our calculations of a-Zr.

FIGURE CAPTIONS

Figure 1. Total density of states in a-Zr. In dashed line we show results which were obtained using potential parameters of pure hcp Zr for all sites. In full lines we show the converged results. The energy scale is relative to the Fermi level.

Figure 2. (a) Distribution of charge transfer among 40 sites of a-Zr. The empty blocks were obtained with potential parameters of pure hcp Zr. The dashed blocks show the converged results.

(b) Converged electrostatic potential at each non-equivalent site. The electrostatic potential was taken as zero for the initial guess.

Figure 3. Distribution of potential parameters $\overline{C}_d$ (Fig.3a) and $\overline{\Delta}_d$ (Fig 3b)for 40 non equivalent sites in a-Zr after convergence is achieved. The horizontal dashed line corresponds to the values in pure hcp Zr. In fig. 3a, the energy scale for $\overline{C}_d$ was taken relative to the Fermi level.

Figure 4. Results for the LDOS at atom number 6 (Fig. 4a) and atom number 14 (Fig. 4b) obtained with parameters of hcp Zr (dashed lines). In full lines we show the final converged results for the same atoms. In both cases the energy is taken relative to the Fermi level.

Fig 1

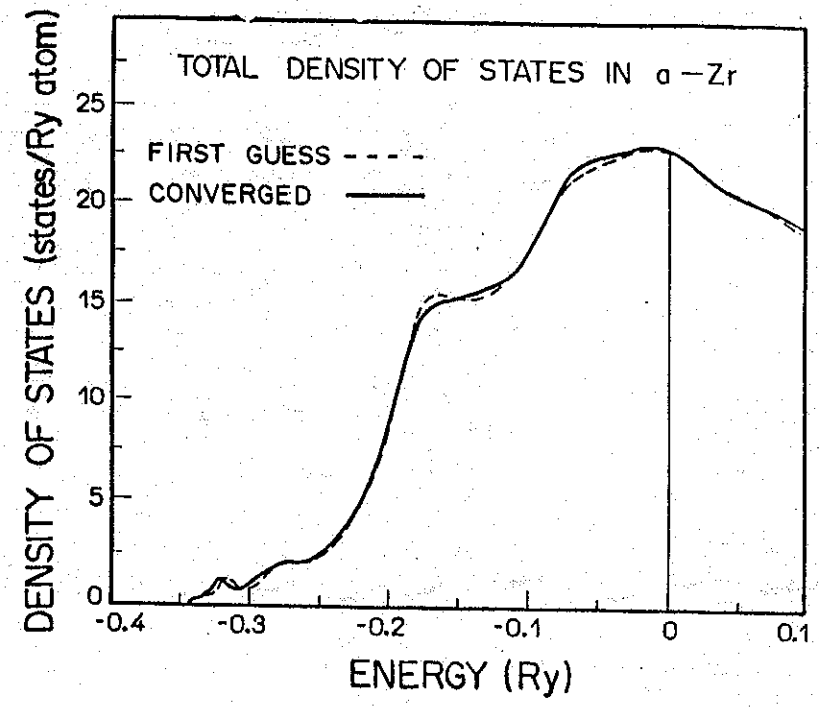
TOTAL DENSITY OF STATES IN α—Zr
FIRST GUESS
CONVERGED
DENSITY OF STATES (states/Ry atom)
ENERGY (Ry)
0
5
10
15
20
25
-0.4
-0.3
-0.2
-0.1
0
0.1

Fig 2.a

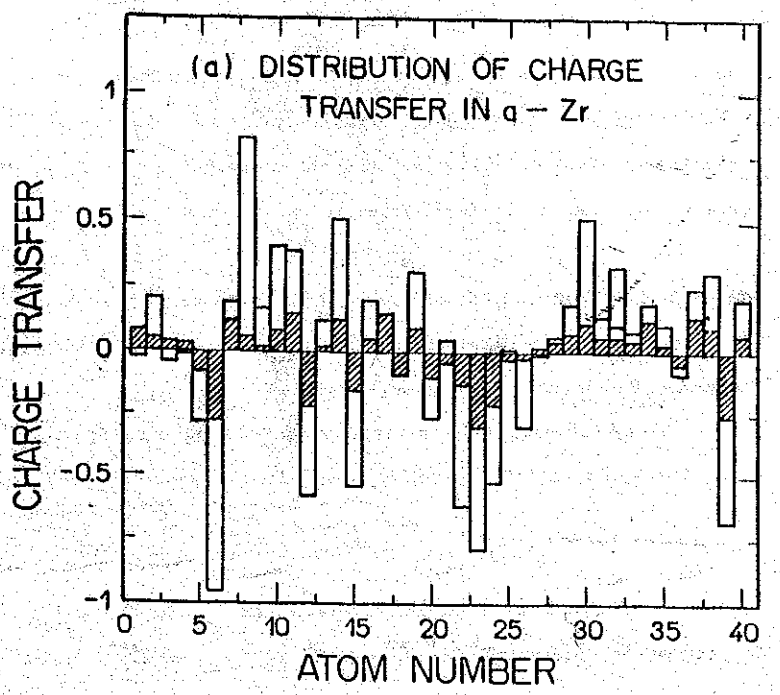
(a) DISTRIBUTION OF CHARGE TRANSFER IN α — Zr
CHARGE TRANSFER
ATOM NUMBER
1
0.5
0
-0.5
-1
0
5
10
15
20
25
30
35
40

Fig 2.b

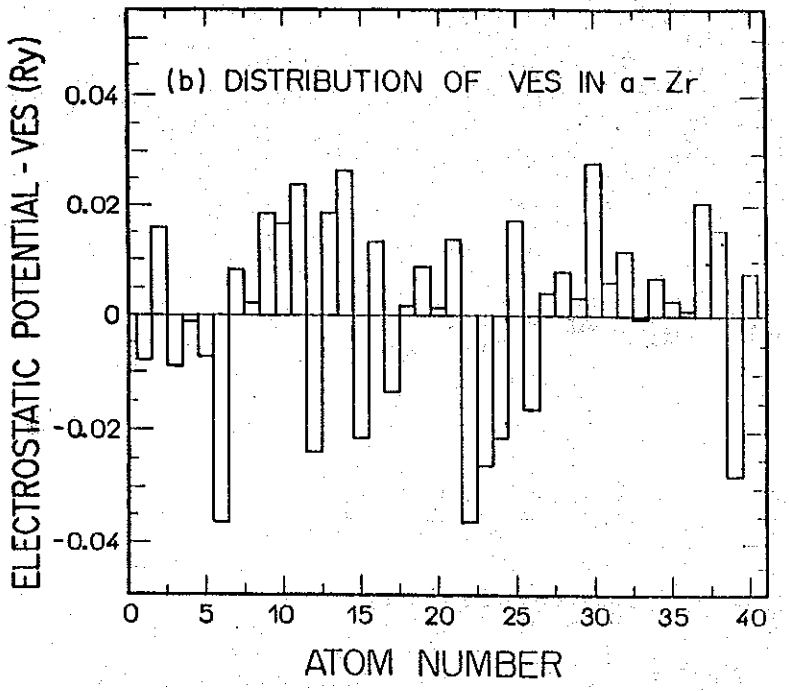
(b) DISTRIBUTION OF VES IN a - Zr
ELECTROSTATIC POTENTIAL - VES (Ry)
0.04
0.02
0
-0.02
-0.04
0
5
10
15
20
25
30
35
40
ATOM NUMBER

Fig 3.a

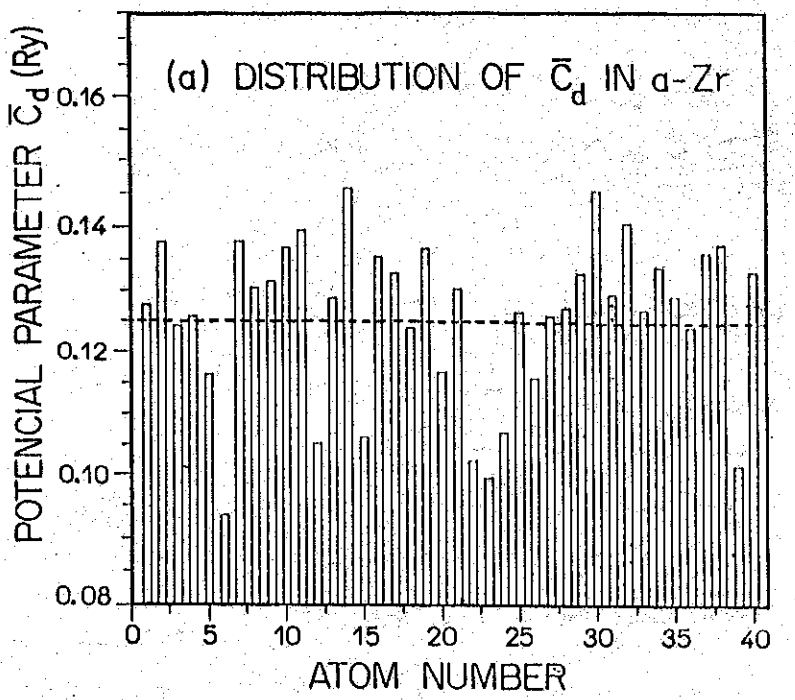
(a) DISTRIBUTION OF $\bar{C}_d$ IN a-Zr
POTENCIAL PARAMETER $\bar{C}_d$ (Ry)
0.16
0.14
0.12
0.10
0.08
0
5
10
15
20
25
30
35
40
ATOM NUMBER

Fig 3.b

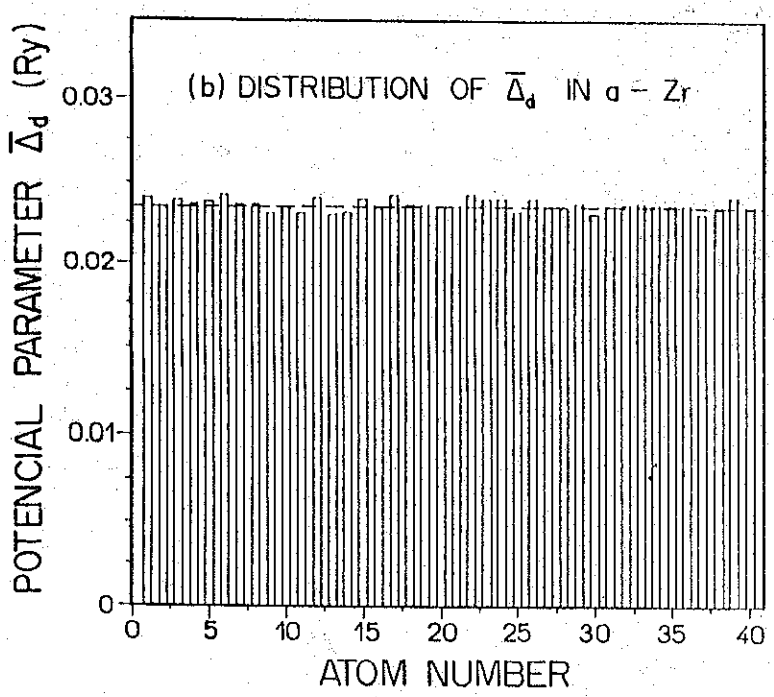

Fig 4.a and 4.b