

Order- N Green's Function Technique for Local Environment Effects in Alloys

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We have developed a new approach to the calculations of ground state properties of large crystalline systems with arbitrary atomic configurations based on a Green's function technique in conjunction with a self-consistent effective medium for the underlying randomly occupied lattice. The locally self-consistent multiple scattering method and the coherent potential approximation are two simple limits of our general formulation. The efficiency and the excellent convergence properties of the method are demonstrated in calculations for two alloy systems, Cu-Zn and Rh-Pd. [S0031-9007(96)00336-5]

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First-principles investigations of the phase stability of materials require an accurate description of the ground state properties of systems with an arbitrary atomic occupation of the underlying crystal lattice. The obvious solution is to consider a large supercell with periodic boundary conditions and apply conventional band-structure methods. However, in that case the computational effort increases with the number of atoms N in the supercell as N^3 , which at present limits the cell size to a few hundred atoms, and an intensive search for techniques with better scaling properties is therefore in progress. One particularly interesting approach is the locally self-consistent multiple scattering (LSMS) method recently outlined by Wang *et al.* [1]. Its central idea originates from the observation that the electron density and the density of states on a particular atom within a large condensed system can be obtained with sufficient accuracy by considering only the electronic multiple scattering processes in a finite spatial region, the so-called local interaction zone (LIZ), centered at that atom. Thereby the solution of the electronic-structure problem for an N -atomic system is decomposed into N locally self-consistent problems including only the M atoms in the LIZ associated with each atom in the system, and the total computational effort now scales linearly with N , i.e., exhibits $O(N)$ scaling. The LSMS method has been used to calculate the ordering energy in β -brass [1] as well as the Madelung energy for a number of random fcc and bcc Cu-Zn alloys [2]. In these calculations it turns out that in order to obtain a 0.1 mRy accuracy in the total energy the local interaction zone must include of the order of 100 atoms. Hence, the LSMS method becomes more efficient than conventional band-structure techniques only for systems containing several hundred atoms, and needs to be implemented on a most powerful supercomputer.

In this Letter, we present a locally self-consistent Green's function (LSGF) approach to the electronic-structure problem which preserves the central idea of the

LSMS method in the form of a local interaction zone. However, instead of solving the real-space multiple-scattering equations we solve the Dyson equation for Green's function of each LIZ embedded in an effective medium. Since the Dyson equation is exact, this effective medium is used only to improve the convergence in real space, i.e., reduce the size of the local interaction zone, and may be chosen in a number of ways. For instance, one may apply a jellium model of some density. This has the advantage of being structureless in real space, and one may recover the LSMS method as the free-electron limit of our method. Alternatively, one may apply the coherent potential approximation (CPA) to the underlying randomly occupied lattice in which case the convergence of the Dyson equation is greatly enhanced. This choice has the further advantage of retaining Fermi surface effects for random alloys. Finally, by restricting the interaction zone to a single site the LSGF method with this particular choice of effective medium reduces to the CPA but with a proper treatment of the Madelung contribution to the total energy.

Three factors contribute to the efficiency of the LSGF method as implemented here. First, the local interaction-zone approach leads to an $O(N)$ scaling of the computational effort. Second, the application of a judiciously chosen effective medium leads to a minimal size of the local interaction zone. Third, the application of a tight-binding linear muffin-tin orbital (TB-LMTO) basis in conjunction with the atomic sphere approximation (ASA) [3] as usual reduces computer time by 1 to 2 orders of magnitude without significant loss of accuracy. Finally, we note that our method is as amenable to parallelization as the LSMS method although this was not necessary for the applications presented here.

The key quantity in the present approach is the on-site block g_{RR} of the Korringa-Kohn-Rostoker-ASA Green's function matrix which is used to construct the charge density in the entire system. Following Lifshitz [4] this

Green's function matrix for the central atom at R in each local interaction zone may be found from the Dyson equation

$$g_{RR} = \tilde{g}_{RR} + \sum_{R'=1}^M \tilde{g}_{RR'}(\tilde{P}_{R'} - P_{R'})g_{R'R} \quad (1)$$

when the LMTO-ASA potential function $\tilde{P}_{R'}$ for the effective scatterers is known. One observes that although the off-diagonal blocks of the desired Green's function matrix $g_{RR'}$ may be long ranged this becomes irrelevant for the on-site matrix if an effective medium can be found such that $\tilde{g}_{RR'}$ has short range in which case the sum over lattice sites may be restricted to a finite cluster, i.e., a local interaction zone, containing M atoms.

Before we specify the effective medium we note that the potential function \tilde{P} for the effective scatterers is the same on all the sites in the system [5]. Therefore the effective medium Green's function matrix \tilde{g} may be obtained from the solution to the electronic-structure problem corresponding to the underlying primitive unit cell rather than the whole N -atomic supercell, i.e.,

$$\tilde{g}_{RR'} = (V_{BZ})^{-1} \int_{BZ} d\mathbf{k} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} [\tilde{P} - S(\mathbf{k})]^{-1}, \quad (2)$$

where $S(\mathbf{k})$ is the TB-LMTO structure constant matrix for the primitive lattice and V_{BZ} the volume of the corresponding Brillouin zone.

If one deals with an alloy problem, it is well known that the best single-site effective medium is given by the CPA [6,7]. Therefore we suggest to determine the potential function \tilde{P} for the effective scatterers which enters the cluster Dyson equation (1) from the CPA-like condition

$$\tilde{g}_{RR} = \langle g_{RR}^0 \rangle = (N)^{-1} \sum_{R=1}^N g_{RR}^0, \quad (3)$$

where \tilde{g}_{RR} is the on-site block of the effective medium Green's function matrix calculated from (2) and g_{RR}^0 is the Green's function matrix for the atom on site R determined from the single-site Dyson equation [9]

$$g_{RR}^0 = \tilde{g}_{RR} + \tilde{g}_{RR}(\tilde{P} - P_R)g_{RR}^0 \quad (4)$$

corresponding to the CPA for multicomponent systems. The potential function for the effective scatterers, i.e., the coherent potential function \tilde{P} , may now be found by iterative solution of Eqs. (2)–(4) until the condition (3) is fulfilled [8].

Following the CPA cycle \tilde{P} is used together with an ansatz for P_R in the cluster Dyson equation (1) to determine the Green's function matrices g_{RR} for all N atoms in the supercell which in turn are used in the conventional manner [9] to determine the Fermi level from the charge neutrality condition for the entire supercell and to construct a new charge density and atomic potential functions P_R . Thereby, the Madelung contribution to the one-electron potential and the total energy is calculated directly from the charge distribution in the N -atomic su-

percell and does not rely on models such as those proposed by Lu *et al.* [10] and by Korzhavnyi *et al.* [11]. The complete procedure starting with the determination of \tilde{P} is finally repeated until a self-consistent total energy is obtained. We refer to our method with this particular choice of effective medium as the LSGF-CPA.

We may now discuss the real-space convergence properties of the cluster Dyson equation (1), i.e., the size M of the LIZ. If the supercell contains only one kind of atom, one immediately finds in the LSGF-CPA that $\tilde{g}_{RR} = g_{RR}^0 = g_{RR}$ and one may use a single-site LIZ to obtain the correct g_{RR} . This should be contrasted with the not less than seven coordination shells needed in the LSMS to calculate pure metals [1]. When the atoms in the supercell are different the size of the LIZ is less obvious and must be determined numerically. However, the Green's function for the CPA effective medium decays, apart from an oscillating factor, exponentially as $R^{-1}e^{-R/l}$, where l is the mean free path [12], and thereby leads to a minimal LIZ. With the free-electron effective medium used in the LSMS method l diverges and the decay is only R^{-1} , which explains the large LIZ used in the LSMS calculations [1,2]. Note that while both the LSMS and LSGF methods are of $O(N)$ they still scale as M^3 and therefore the application of a CPA effective medium reduces computer time by 3 orders of magnitude.

The excellent real-space convergence of the LSGF-CPA method may be judged from Fig. 1 where we show

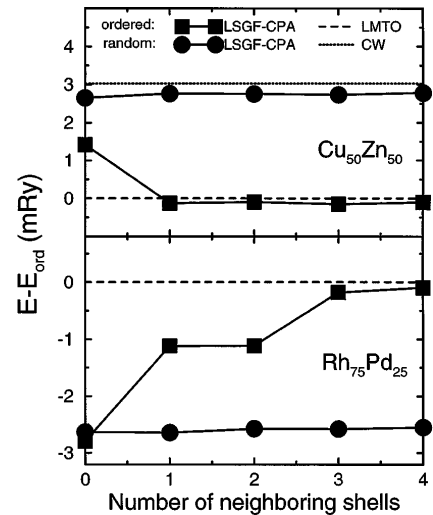


FIG. 1. Convergence of the total energy of Cu-Zn and Rh-Pd alloys as a function of the number of neighboring shells included in the local interaction zone. Values obtained by the LSGF-CPA method for random and ordered ($L1_0$ for CuZn, $L1_2$ for Rh₃Pd) structures are shown by filled circles and squares, respectively. For comparison we also include values obtained for the ordered structures by LMTO bulk calculations, dashed lines, and for random structures by the Connolly-Williams method, dotted lines. For Cu₅₀Zn₅₀ we used 144 atoms in the supercell and for Rh₇₅Pd₂₅ 256, but a reduction of these numbers to 72 atoms per cell changes the total energies by less than 0.1 mRy.

the total energy of fcc $\text{Cu}_{50}\text{Zn}_{50}$ and $\text{Rh}_{75}\text{Pd}_{25}$ alloys which have been chosen as examples of systems with ordering tendency, Cu-Zn, and a miscibility gap, Rh-Pd. These two systems have been modeled by supercells containing 144 and 256 sites, respectively, on the underlying fcc lattice and the atoms distributed according to two particular choices of the short-range order parameters, one corresponding to a completely random phase and the other to a completely ordered phase. It is seen that convergence for the random alloy systems is reached already for a single-site local interaction zone indicating that the CPA effective medium is a particularly good choice in this case. For the ordered alloys we find that the Cu-Zn system requires a local interaction zone of only one coordination shell while Rh-Pd requires four coordination shells for complete, less than 0.1 mRy, convergence. This latter finding is in agreement with the observation that the effective pair interactions in Rh-Pd are nonzero up to four coordination shells [13], but are short ranged in Cu-Zn [14]. In fact, one may show that the size of the LIZ to be used in LSGF-CPA calculations for nonrandom distributions of atoms corresponds roughly to the range of these effective pair and multiatom interactions.

The Connolly-Williams (CW) method [15] represents an alternative approach which has been used with considerable success in the calculation of total energies of random alloys. Here, it is used to obtain the total energy of random $\text{Cu}_{50}\text{Zn}_{50}$ based on the total energies of five ordered Cu-Zn alloys. The results are included in Fig. 1, and the excellent agreement with our LSGF values demonstrates the reliability of the two alternative approaches. However, we note that in the CW method all information about the electronic structure is lost and to extract any spectral information one must use methods such as the LSGF-CPA which preserve that information.

Based on timings of our LSGF-CPA and LMTO band calculations including suitable k -space samplings we have estimated the size N_c of the supercell where the LSGF-CPA becomes the more efficient technique. We find that for a local interaction zone of one coordination shell, which is the case for Cu-Zn, $N_c = 2$ and for a zone of four shells, which is the case for Rh-Pd, $N_c = 45$. Since it is to be expected that the description of an alloy system, with short-range order, in the complete concentration range requires supercells with of the order of 100 atoms it follows that we are always in the regime where the LSGF-CPA will be the most efficient first-principles technique.

We have applied our LSGF-CPA method in the calculation of the mixing enthalpies of α -CuZn considering random and ordered phases as well as phases with short-range order. The alloy systems were modeled by a 72-atom supercell and the local interaction zone included one shell of nearest neighbors, i.e., 13 atoms in total. We have tested the convergence of the calculations and find that the total energy per atom changes much less than 0.1 mRy when the number of atoms in the supercell is

increased from 32 to 144. This is in agreement with an earlier observation that a supercell of about 100 atoms should be sufficient to model a random alloy, provided the atomic distribution is chosen such that the pair correlation functions are correct for the first few coordination shells [1,16].

In Fig. 2 we present the total energy of ordered and random $\text{Cu}_{75}\text{Zn}_{25}$ as a function of lattice spacing. We note the perfect agreement with bulk LMTO calculations for the ordered structure and with CW calculations for the random structure. Furthermore, the description of charge transfer effects included in the LSGF-CPA method leads to improved, i.e., lower, total energy of the random phase relative to the conventional CPA results. Also, we observe that the LSGF-CPA gives an accurate description of ordering phenomena. Finally, Fig. 2 is one example of a series of total-energy curves needed to derive the mixing enthalpy of α -CuZn over the complete concentration range. At each concentration one must minimize the total energy with respect to the lattice spacing and subtract the energy of the reference state to obtain the enthalpy.

The mixing enthalpies of α -CuZn alloys were first calculated in the framework of the local density approximation and the CPA by Johnson *et al.* [17] who found values which were less negative than the experimental data [18] but with correct concentration dependence. In Fig. 3 we show similar results obtained by conventional CPA which illustrate the above statement. It is now well known [11,19–21] that part of the discrepancy between theory and experiment is due to the neglect of charge transfer effects in conventional CPA, and it is expected that the remaining discrepancy is caused by short-range order (SRO) effects also neglected in the CPA. To investigate this expectation we have calculated the mixing enthalpies for random Cu-Zn with short-range order. The actual value of the SRO parameter was obtained by the cluster variation method

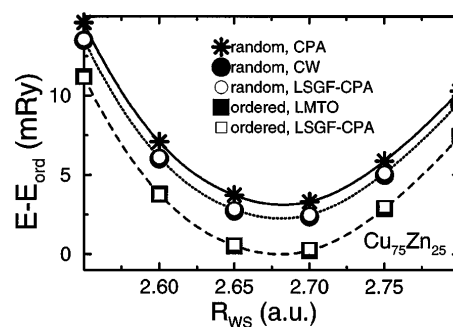


FIG. 2. Total energies of random and ordered ($L1_2$ structure) $\text{Cu}_{75}\text{Zn}_{25}$ alloys as a function of the Wigner-Seitz radius R_{ws} obtained by different computational techniques. The LSGF-CPA results are shown by open circles (completely random alloys) and open squares (ordered compounds). The results for the random alloys obtained by the CW method are shown as filled circles, and the results from conventional LMTO Green's function calculations for the ordered phases are given by filled squares. The CPA results for the random alloy are shown by stars.

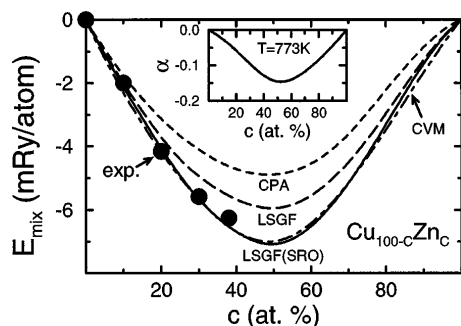


FIG. 3. Mixing energies E_{mix} for fcc Cu-Zn alloys as a function of Zn concentration c . Values for the random alloy with SRO corresponding to $T = 773$ K have been calculated by the LSGF-CPA method (full line) and by the cluster variation method (CVM, dot-dashed line). The experimental data measured at the same temperature [18] are indicated by filled circles. The mixing energies for the completely random alloy, calculated by LSGF-CPA and by the conventional CPA methods, are shown as a long-dashed and dashed lines, respectively. The inset shows the Warren-Cowley SRO parameter $\alpha_{\text{Cu-Zn}}$ for the first nearest neighbors obtained by the CVM-CW method at 773 K and used in LSGF-CPA calculations for the alloys with SRO.

(CVM) [22] and CW interactions for each concentration considered here (10%, 20%, 25%, 30%, 40%, 50%, 75%, and 90%) and at 773 K which is the temperature at which the experimental mixing enthalpies were measured. After that Cu and Zn atoms were distributed in the supercell according to the so obtained SRO parameters, and the LSGF-CPA calculations performed. The resulting mixing enthalpies are shown in Fig. 3 and it is gratifying to note that not only do we find complete agreement with the alternative CVM-CW calculations but also with the experimental values. We view this as a manifestation of the accuracy of the LSGF-CPA method and of the underlying local density approximation.

In summary, we have introduced the LSGF method which may be used in first-principles calculations of the electronic properties of large systems with broken three-dimensional symmetry. The method is based on the Dyson equation for a cluster Green's function the dimension of which is reduced to a minimum due to a judicious choice of effective medium. It exhibits $O(N)$ scaling in the system size and may be more efficient than conventional band-structure methods already for N as small as 2–4 atoms per cell. We have demonstrated that the LSGF results for ordered and random alloys agree with alternative one-electron methods as they should. The method has been applied to calculate the mixing enthalpy for α -CuZn with short-range order and the results are in excellent agreement with experiment.

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