The mathematics of the polymorphous coherent potential approximation

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Abstract
The original coherent potential approximation (CPA) used for calculating the electronic states in substitutional solid-solution alloys contains the implicit assumption that the alloy is isomorphous. That is, all of the atoms of a given chemical type are assumed to be identical. The extension of the CPA philosophy to treat an alloy model in which all of the atoms are allowed to have distinct charges and potentials is called the polymorphous CPA (PCPA). This extension requires some interesting changes in the mathematical formalism that is used to develop the CPA equations. Aspects of the mathematical formalism of the PCPA will be discussed. In particular, the ergodic theorem from measure theory will be invoked to justify the new equations for the average Green's function.

1. Background

The polymorphous coherent potential approximation (PCPA) is a theory used for calculating the one-electron states of a disordered substitutional alloy in which several different kinds of atom are distributed randomly on the sites of an underlying Bravais lattice. It differs from the traditional isomorphous coherent potential approximation (CPA) [1] by allowing every atom to have a different charge density. In the isomorphous model, the atoms of a given chemical type are assumed to be identical. The PCPA treats the Coulomb effects in metallic alloys better than any isomorphous CPA, as has been demonstrated in previous publications [2, 3]. In a PCPA calculation, a supercell containing a large number N of atoms is generated. Averages taken over the sites of the supercell are used instead of the ensemble averages used in the CPA. Questions have arisen concerning this and other new features of the PCPA. The purpose of the present paper is to address these mathematical questions in more detail.

The volume of an alloy Ω may be divided into N non-overlapping unit cells Ω_i so that $\Omega = \sum_i^N \Omega_i$. The nucleus of the ith atom is at the centre of Ω_i. Within the local density

approximation (LDA) [4], the one-electron potential function can always be written as a sum of non-overlapping potentials that are associated with each unit cell Ω_i:

$$v(\boldsymbol{r}) = \sum_{i=1}^{N} v_i(\boldsymbol{r}). \tag{1}$$

In early theories for the electronic structure of alloys it is assumed that $v(\boldsymbol{r})$ is given, and the only problem to be addressed is that of finding the solutions for the Schrödinger equation. These theories all focus on an isomorphous model of the alloy in which, for the binary alloy, $v_i(\boldsymbol{r}) = v_A(\boldsymbol{r})$ when there is an A atom in unit cell i, and $v_i(\boldsymbol{r}) = v_B(\boldsymbol{r})$ when there is a B atom in the unit cell. This is true of the virtual-crystal approximation [5] and the average t-matrix approximation [6] as well as the CPA [1]. There were many reasons for this assumption, not the least important of which is that the task of solving the Schrödinger equation without the help of Bloch's theorem is daunting enough without worrying about additional complications.

The proper application of the LDA requires that the potential $v(\boldsymbol{r})$ must be calculated self-consistently. In the case of a band theory calculation for a periodic solid, a self-consistent calculation simply requires more computer time than a non-self-consistent one. However, for disordered alloys, the addition of a self-consistency step introduces profound problems into the theory because of the Madelung shifts arising from the long-range Coulomb interaction with the atoms in the other unit cells.

Coulomb effects can be visualized easily by considering ordered intermetallic compounds. Subtracting the charge on the nucleus Z_i in Ω_i from the total electronic charge in that cell gives a net charge q_i. The total crystal must be charge neutral, so the positive charges on the A sites must by cancelled by negative charges on the B sites, but the charges create electrostatic potentials. These Madelung contributions to the A and B potentials can be calculated easily for ordered compounds.

There are net charges q_i in the unit cells in disordered alloys, and hence there will be Madelung shifts contributing to each of the $v_i(\boldsymbol{r})$. It is apparent after a moment's reflection that any theory that includes the Madelung shifts correctly will be inconsistent with the iso-morphous model of an alloy. Picture an alloy in which A and B atoms are distributed randomly on the sites of a Bravais lattice. Assume that the alloy is isomorphous so that the net charge on every A site is q_A and that on every B site is q_B. Now imagine a calculation of the electrostatic potentials at each site. It is clear that the shifts will be different at each site, and hence the $v_i(\boldsymbol{r})$ are different at each site, which contradicts the original isomorphousness assumption.

This simple argument became apparent when self-consistency was considered, but, by that time, the notion that an isomorphous model is an essential assumption in CPA theory was implanted. The derivation of the first theory that included self-consistency in the CPA, the KKR-CPA [7], led to the result that the Madelung potential in the alloy must be zero. This is the correct answer, given the assumptions, because it is the only way to obtain a self-consistent model that is isomorphous. However, it is inconsistent that the theory predicts charge transfer and a zero Madelung potential at the same time.

By giving up the assumption of an isomorphous model, the PCPA is able to treat Coulomb effects without difficulty. However, the earlier versions of the CPA have been very successful in explaining the properties of disordered substitutional alloys, and there are worries that some of the useful features of the CPA approach will be lost in the PCPA. There are also questions about the size of the errors in isomorphous CPAs and whether or not they necessitate a shift to the polymorphous model. In section 2, new computational results are shown that illustrate the long-range nature of the Coulomb potential in metallic alloys in ways that are different from the discussions in previous publications. Some of these calculations address specific questions

that have been brought up. The site-average method for averaging the Green's function that is required in the derivation of the PCPA is justified using the mathematical ergodic theory in section 3.

2. The Coulomb energy of metallic alloys

The nature of the Coulomb energy in metallic alloys has been studied extensively [8, 9] using the locally self-consistent multiple-scattering (LSMS) method [10]. This is an order-N method for carrying out LDA calculations on supercells containing a large number N of atoms. Order-N methods have the property that the amount of CPU time required for the self-consistent calculation scales as N rather than N^3, as is the case for conventional methods.

Figure 1 shows the distribution of charges on the copper and zinc sites in a 50% alloy with a bcc Bravais lattice. The supercell contains 1024 atoms, and each histogram box shows the number of atoms having a charge within the indicated range of 0.01 electron charges. The copper atoms take on a positive number of electron charges, as shown in the figure, which means that they are negatively charged. The details of the calculations on this model of β-brass have been published [9]. Figure 1 illustrates that the isomorphous model, which would predict a charge of $\pm 0.099\,78$ on every copper and zinc atom, is completely incorrect for this realistic model of an alloy.
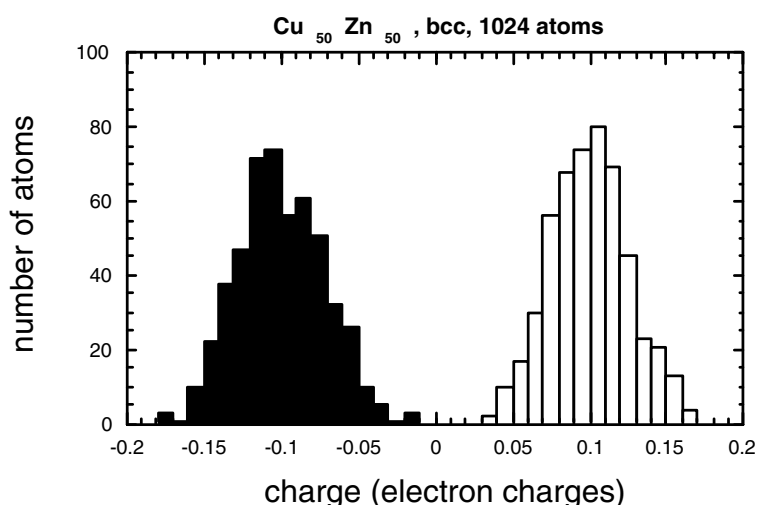
Figure 1. The distribution of charges on the sites of a 50% copper–zinc alloy modelled with a supercell that contains 1024 atoms. The charges on the 512 copper sites are shown by the white histogram, and the charges on the 512 zinc sites are shown in black.

The fact that every atom in the alloy has a different charge, as illustrated in figure 1, demonstrates that the Madelung shift at a site includes contributions from atoms that are infinitely far from the site. This follows from the fact that no two sites have the same neighbourhood if the radius that defines the neighbourhood is allowed to increase to infinity. This simple result seems to violate the intuition of some people in the alloy theory community, and has been questioned formally in publications [11] as well as informally in private communications. For this reason it deserves more discussion.

2.1. The range of contributions to the Madelung potential at a site

The most direct way to address the question of the long-range nature of the Coulomb interaction in alloys is to analyse further the data generated in the calculation on the model of a 50% copper–zinc alloy that was discussed above. Let us consider the contributions to the Madelung potential at a site i from the atoms within a sphere of radius r:

$$V^i(r) = \sum_{r_{ji} \leqslant r} \frac{2q_j}{r_{ji}} \qquad (2)$$

where $r_{ji} = |\mathbf{R}_j - \mathbf{R}_i|$. Since the atoms are on a Bravais lattice, this sum changes only when r is equal to the radius of some nearest-neighbour shell r_n. All of the data needed for the calculation of the sum in equation (2) can be taken from the 1024-atom supercell calculation [9]. The function $V^{513}(r)$ that gives the sum of contributions for site 513, which happens to contain a copper atom, is shown in figure 2. The value, $V^{513}(\infty)$, that this function should attain as r approaches ∞, calculated by the Ewald method, is also shown. The figure shows contributions from the first 51 nearest-neighbour shells. Clearly, there is no short-range convergence of this sum.
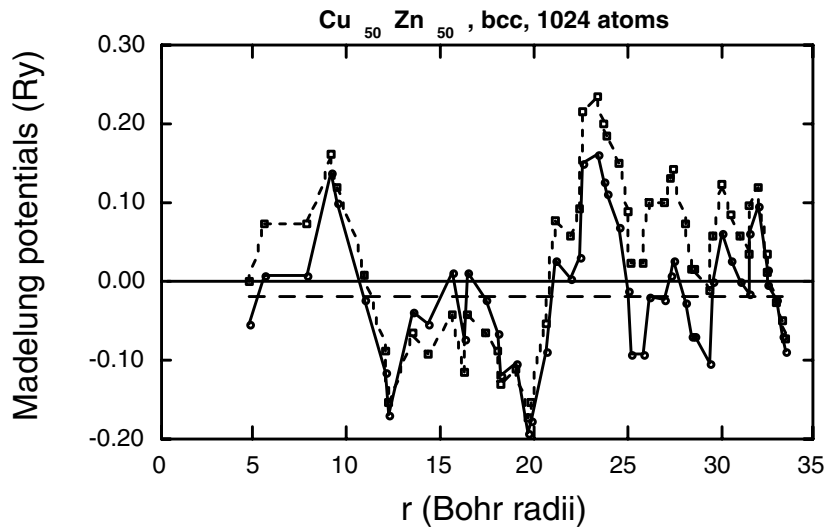
Figure 2. The contributions to the Madelung potentials as a function of r for a 50% bcc copper–zinc alloy modelled with a supercell that contains 1024 atoms. The circles connected with the solid line indicate the contributions to site 513, $V^{513}(r)$. The squares connected with the dotted line show the contributions for the hypothetical isomorphous model, $V_{iso}^{513}(r)$. The straight dashed line shows the asymptotic value $V^{513}(\infty)$.

To get more insight into this result, we show in figure 2 the value that the sum would have, $V_{iso}^{513}(r)$, for a hypothetical isomorphous alloy in which $q_j = 0.099\,78$ if there is a copper atom on site j, and $q_j = -0.099\,78$ if there is a zinc atom on that site. The sum $V_{iso}^{513}(r)$ looks very much like $V^{513}(r)$, although there are some subtle differences that will be discussed later. We will first explain the shape of $V_{iso}^{513}(r)$, because it is the easiest to describe. The number of atoms in the shell $r \leqslant r_{ij} \leqslant r + \delta$ is $N_\delta(r) = n(r)\delta$, where $n(r) = \rho 4\pi r^2$, ρ is the density of atoms in the crystal, and δ is a small but fixed thickness. When $N_\delta(r)$ is large enough that the central-limit theorem can be used, it is known that the root mean square deviation of the number of A atoms in the shell about the average value $\overline{n_A} = c_A N_\delta(r)$ is

$\sigma_\delta(r) = \sqrt{c_A(1 - c_A)N_\delta(r)}$, where c_A is the concentration of A atoms. The fluctuation in the charge within the shell is proportional to r. It follows that the contribution to $V_{iso}^{513}(r)$ from charges in the shell fluctuates around the values $\pm 0.099\,78\sqrt{c_A(1 - c_A)4\pi\rho\delta}$, which are independent of r. This predicts that the shape of $V_{iso}^{513}(r)$ is the same as would be obtained by summing a set of contributions $\pm\epsilon$, where a coin is flipped and the $+\epsilon$ is added when the coin shows heads and $-\epsilon$ is added when it shows tails. This coin flip calculation can easily be done on a computer using a random-number generator, and, as expected, the resulting output looks very similar to $V_{iso}^{513}(r)$.

According to this algebra, the contributions to $V_{iso}^{513}(r)$ from distant shells will continue as shown in figure 2 forever. The shape of $V^{513}(r)$ is explained in a similar way, but there is an additional statistical step because the distribution of charges on the Cu and Zn atoms must be obtained from figure 1.

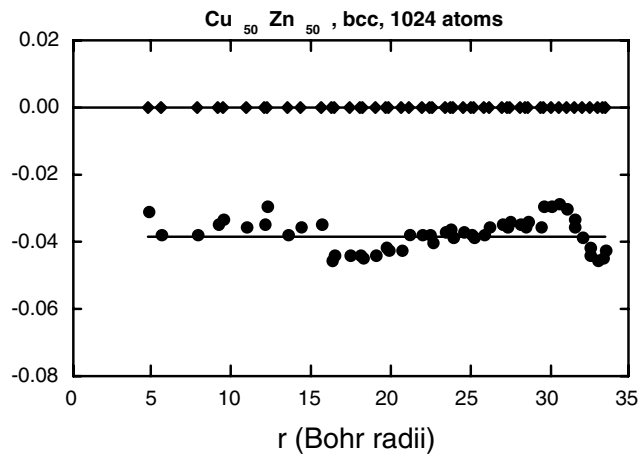### 2.2. The average of the Madelung potentials for one species of atom

The $V^i(r)$ that are defined in equation (2) and shown in figure 2 have been averaged over all the 512 sites in the supercell that contain a copper atom:

$$V^{Cu}(r) = \frac{1}{c_{Cu}N} \sum_{i \subset Cu} V^i(r). \tag{3}$$

The average $V^{Cu}(r)$ is compared with the average of the exact Madelung potentials:

$$V^{Cu}(\infty) = \frac{1}{c_{Cu}N} \sum_{i \subset Cu} V^i(\infty) \tag{4}$$

in figure 3. There is some scatter, but it appears that $V^{Cu}(r) = V^{Cu}(\infty)$ when r is equal to the radius of the second-nearest-neighbour shell. The average of the hypothetical isomorphous potentials $V_{iso}^{Cu}(r)$ can be shown both algebraically and numerically to be equal to zero for all r. This is also indicated in figure 3, and is consistent with the derivation of the KKR-CPA.

Figure 3. The average of the contributions to the Madelung potentials as a function of r for a 50% bcc copper–zinc alloy modelled with a supercell that contains 1024 atoms. The circular dots indicate the contributions $V^{Cu}(r)$, and the straight line shows the asymptotic value $V^{Cu}(\infty)$. The diamond-shaped dots show the average of the contributions for the hypothetical isomorphous alloy, $V_{iso}^{Cu}(r)$.

2.3. Madelung shifts in ordered alloys

It can be seen from the preceding discussion that the charges on all the other atoms in the crystal contribute to the Madelung potential at a site in a disordered alloy. There is no screening of the charges, because all the atoms are charged. The problem of a single impurity in an otherwise perfect crystal should therefore not be used for guidance in dealing with the alloy, as has been proposed in the literature. Coulomb effects in disordered alloys have much more in common with those in ordered alloys.

The calculation of the Madelung potential for simple ordered crystal structures is discussed in most elementary texts on solid-state or condensed matter physics. It is pointed out that the sum in equation (2) is only conditionally convergent, and cannot be evaluated directly. An elegant and exact method for calculating the sum was introduced by Ewald [12]. Although Ewald solved the problem, it was thought that a brute-force method would be easier to understand. The sum can be evaluated by rearranging the atomic positions into clusters. Fractional charges are put on the atoms in a cluster in such a way that each cluster is charge neutral. The sum of these charge-neutral clusters is convergent. The textbooks state that a rough approximation to the Madelung potential can be obtained by summing a relatively small number of the clusters. Unfortunately, this can lead to the misconception that only a few atoms in the neighbourhood of the site are responsible for the Madelung potential in an ordered crystal. It is not necessary to rely on second-hand discussions to understand the Coulomb calculations on ordered crystals. Programs are widely available for evaluating the Madelung potential by the Ewald method. Calculations with the cluster methods were major undertakings in the 1930s when they were first done, but today they can be programmed and carried out on a PC with Linux with little effort.

For the purpose of understanding Coulomb energies in ordered crystals, the most informative ordered crystal to study is the caesium chloride (CsCl) or B_2 structure. The Madelung potential can be written as

$$V^i(\infty) = \pm\alpha\frac{q^2}{R_{nn}} \tag{5}$$

where R_{nn} is the radius of the first-nearest-neighbour shell and q is the net charge on a site. The parameter α is called the Madelung constant. Using the Ewald method [12], we calculate $\alpha = 1.762\,6748$ for CsCl. The proper cluster method for calculating α is due to Höjendahl who used a charge-neutral dodecahedron that has 15 sites [13]. A charge of 1.0 is put on the site $\{0, 0, 0\}$, charges of -0.5 are put on the eight sites that can be obtained by choosing all possible + and − signs for vectors of the form $\{1, 1, 1\}$, and charges of 0.5 are put on the six sites that can be obtained by permuting and using + and − signs on vectors of the form $\{2, 0, 0\}$. Counting the fractions, there are eight atoms in a dodecahedron. Supercells are created by placing the centres of these dodecahedra on the sites of a bcc Bravais lattice with basis vectors $\{2, 2, -2\}$, $\{2, -2, 2\}$, and $\{-2, 2, 2\}$. When many clusters are included in a supercell, the charges on the internal atoms are all $+1.0$ or -1.0. The only atoms with fractional charges are on the surface. The sum of the contributions to α from the 14 fractional charges that surround the central atom in a dodecahedron is 1.401\,9238. Augmenting this central cluster with the 26 clusters that adjoin it, we get 1.747\,5750 for α. There are 216 atoms in this supercell, and α is not too far from the exact value. This is what the textbooks mean by a rapidly converging series. Of course, for modern total-energy calculations, an α that is incorrect in the second decimal place is useless. Including 1\,030\,301 clusters or 8\,242\,407 atoms in the sum leads to $\alpha = 1.762\,6584$, which is correct to four decimal places. This is still not good enough for modern calculations, and, unfortunately, including more clusters in the sum does not help. The sum actually diverges slowly away from the correct answer as

more clusters are included. This is one of the reasons that the cluster method is not used in any modern band theory programs.

Prior to Höjendahl's calculations, Evjen had attempted to use a cluster method to calculate the Madelung constant for CsCl [14]. He had success calculating α for the NaCl lattice, but he focused on cubic clusters. Evjen's first cluster has nine sites. A charge of 1.0 is placed at $\{0, 0, 0\}$, and charges of -0.125 are placed on the eight sites that are generated from the vector $\{1, 1, 1\}$. Including 8 120 601 of these clusters on the sites of a cubic Bravais lattice with unit vectors $\{2, 0, 0\}$, $\{0, 2, 0\}$, and $\{0, 0, 2\}$, or 16 241 202 atoms, gives $\alpha = 0.402\,3071$. Evjen tried another cubic cluster made up of 35 sites. A charge of 1.0 is placed on $\{0, 0, 0\}$, charges of -1.0 are placed on the eight sites generated from the vector $\{1, 1, 1\}$, charges of 0.5 are placed on the six sites generated from $\{2, 0, 0\}$, charges of 0.25 are placed on the twelve sites generated from $\{2, 2, 0\}$, and charges of 0.125 are placed on the eight sites generated from $\{2, 2, 2\}$. Including 1 030 301 clusters on the sites of a cubic lattice with lattice vectors $\{4, 0, 0\}$, $\{0, 4, 0\}$, and $\{0, 0, 4\}$, or 16 484 816 atoms, gives $\alpha = 3.122\,9887$. Höjendahl not only found the correct cluster to use, but he pointed out that the average of the values obtained by Evjen is $\alpha = 1.762\,6479$, very close to the value that he obtained. The papers by Höjendahl and Evjen are not easy to obtain. Every aspect of the Madelung potential is treated very thoroughly in the review article by Tosi [15].

The reason for the failure of Evjen's clusters is that the atoms on the surface of the super-cell are all negative for the first cluster, and they are all positive for the second. No matter how many clusters are used, the effects of the surface atoms will never become negligible. Half of the atoms on the surface of the supercell are positive and half are negative when the Höjendahl cluster is used, and this is a better boundary condition. These results demonstrate again the long-range nature of the Coulomb potential.

Why do surface effects not appear in the Ewald calculation? In the Ewald method, a partial transformation is made so that short-range effects are calculated with a real-space sum and long-range contributions come from a reciprocal-space sum. An approximation is made during this transformation that effectively throws out surface effects. This eliminates surface effects for the Coulomb case described here, and it provides a similar service for diffraction calculations and calculations of the lattice constants in the Korringa–Kohn–Rostoker band theory method.

2.4. Possible limitations on the LDA calculations

The authors of this paper were led to the conclusion that Coulomb interactions in disordered alloys are long range by the results of calculations on realistic models using the LSMS. Some who find the results disturbing argue that they are influenced by approximations in the LSMS and in the models [11].

The LSMS is a thoroughly tested order-N method. Infinitely many atoms are used in the calculations, with supercells containing N atoms being periodically reproduced to fill all space. The multiple-scattering equations are solved exactly for the atoms in a local interaction zone (LIZ) surrounding a particular atom. The t-matrices for atoms outside the LIZ are set equal to zero. This process is repeated for each of the atoms in the supercell. The Madelung potentials are calculated exactly for the infinity of atoms using the Ewald method. It can thus be said that the LSMS is of order N as far as the continuity of the wave functions is concerned, but the Coulomb part is not of order N. The Coulomb part is such an easy calculation that it does not matter that it is not simplified. Today the LSMS is being used primarily to study problems in magnetic multilayers [16] and non-collinear magnetism [17].

Another order-N method that is being used for calculations on alloys is the locally self-consistent Green's function (LSGF) method. It differs from the LSMS in that the t-matrices that are outside the LIZ are chosen in some convenient way rather than being set equal to zero [18]. This makes it possible to choose smaller LIZs. The Madelung potential is calculated in the same way as for the LSMS. For the special case where the effective t-matrices are given by a CPA equation and the LIZ is one atom, the LSGF and the PCPA are identical. The LSGF method is better than the LSMS for treating substitutional alloys, but, in the way that it is usually applied, the atoms in the supercell must be on the sites of a periodic Bravais lattice. The atoms can be placed anywhere in the LSMS method, and it has been used for calculations on amorphous solids [19]. Results of calculations on substitutional alloys with the LSMS and LSGF methods are consistent.

Most of the calculations described in this paper use the muffin-tin potential, in which the self-consistent LDA potential is approximated by one that is spherically symmetric within spheres surrounding the nuclei and is constant outside those spheres. It is generally agreed that the muffin-tin approximation does not work well for covalently bonded solids like silicon and germanium. The forces on nuclei calculated with the Hellmann–Feynman theorem tend to be inaccurate when the muffin-tin potential is used [20]. Multiple-scattering calculations can now be carried out in a full-potential mode [21], but a large number of calculations have shown that the muffin-tin approximation will not seriously affect the results for transition-metal alloys quoted here [22].

Muffin-tin calculations require less CPU time than full-potential calculations, and, in addition, many equations derived from multiple-scattering theory are simpler and more transparent when the muffin-tin approximation is used. For example, defining the Janak operator $J(\rho(r))$ by

$$
J(\rho(r)) = -\frac{2}{r} \int_\Omega \rho(r)\, dr + 8\pi \int_0^r dr' \left(\frac{r'^2}{r} - r' \right) \rho_{mt}(r') + 8\pi \int_0^{R^i_{mt}} dr\, r \rho_{mt}(r)
$$

$$
+ \mu_{xc}(\rho_{mt}(r)) - \mu_{xc}(\rho_0) - \frac{4\pi\rho_0}{\Omega_0} \left[\frac{N\alpha^{ii}_M}{2\pi} \Omega^2 + \frac{6\Omega + 4\Omega_0}{5} R^2_{mt} \right]
$$

the potential inside the ith muffin tin sphere can be written as

$$
v^i(r) = J(\rho^i(r)) + 2 \sum_{j=1}^N \alpha^{ij}_M q_j.
$$

The factor 2 arises because $e^2 = 2$ in dimensionless units. The potential is zero when r is in the interstitial region. The Janak operator is identical to the one used to generate the potential for a band theory calculation on a monatomic crystal [23]. The elements of the Madelung matrix α^{ij}_M are calculated by the Ewald method [15], and q_j is the net charge in the jth cell. The factor 2 appears because dimensionless units are being used. The formula for the self-consistent potentials is much more complicated for the non-muffin-tin case.

Another approximation that is used is to ignore static displacements of the atoms in the alloy. From the sharpness of the Bragg peaks and the smallness of the static Debye–Waller factors observed in diffraction experiments on metallic alloys for many years, it is clear that the atoms remain close to the sites of the average lattice. This conclusion is corroborated by the most recent experimental studies [24]. Thermal displacements are also significant. At room temperature, the rms average of the thermal displacements is 3–4 times larger than the rms average of the static displacements, even for alloys with a large size mismatch [25]. Of course, the copper–zinc alloys used for illustrations in this paper have negligible size mismatch.

2.5. Efforts to include Coulomb effects in an isomorphous CPA

The inconsistency in the KKR-CPA theory which predicts both a charge transfer and a zero Madelung potential was pointed out [26]. Efforts were made to remove this inconsistency, but these theories are also based on the assumption of an isomorphous model for the alloy.

The screened-impurity model (SIM) CPA [27] starts from the observation that the charge on a single impurity in an otherwise perfect metallic crystal is screened approximately within the first-nearest-neighbour shell. In the SIM-CPA each atom in the alloy is surrounded by a shell of charge located at the radius of the first-nearest-neighbour shell, R_{nn}, which completely screens the charge on the atom. This simulates the effect of a Madelung potential, and the resulting theory is only slightly more complicated than the KKR-CPA. The contribution to the Coulomb energy that arises naturally in the SIM-CPA is considered to be unsatisfactory, and it is multiplied by a parameter β that cannot be obtained from within the theory [28]. The objection can be raised that this parameter violates the tenets of the LDA since it multiplies the Coulomb contribution to the total energy but it does not appear in the self-consistent potential.

The charge-correlated (CC) CPA [29] starts from a proposal [26] that the charge on an atom in an alloy is proportional to the number of like and unlike atoms in the nearest-neighbour shell. If this idea had been applied consistently, a supercell would have been used and it would have led to a polymorphous CPA that differs from the PCPA only in that the Madelung potential would be calculated approximately instead of exactly. The results of the CC-CPA calculations were seen to be almost the same as those for a screened (SCR) CPA that differs from the SIM-CPA only in that it does not contain the parameter β. The authors conclude that the most useful theory is the SCR-CPA [29].

The advocates of the SIM-CPA and SCR-CPA can take some encouragement from the averaged Madelung potentials such as the $V^{Cu}(r)$ shown in figure 3. The contributions to this Madelung potential seem to be short range. It is only necessary to change the original derivations of the CPAs to include this extra averaging step. On closer inspection, there are still problems. If the isomorphous picture is applied consistently, the average $V^{Cu}_{iso}(r)$ should be used rather than $V^{Cu}(r)$, but $V^{Cu}_{iso}(r) = 0$ for all values of r, as was originally pointed out in the derivation of the KKR-CPA. Overlooking this difficulty and arguing that the isomorphous assumption will only be introduced in the final steps, there is still the problem that $V^{Cu}(r) = V^{Cu}(\infty)$ for some value of r that is greater than R_{nn}. The SIM-CPA and SCR-CPA could be modified by placing the screening shell at a radius other than R_{nn}, but the price for this freedom is that the theories are no longer unique.

A completely different approach the Coulomb problem in alloys is the proposal to use charge-neutral atoms [30]. This theory is based on the observation that the way that the volume of a theoretical model of the alloy Ω is divided into N non-overlapping unit cells Ω_i so that $\Omega = \sum_i^N \Omega_i$ is quite arbitrary. There is always a partitioning of the alloy so that the net charge associated with q^i associated with the cell Ω_i is zero for all i. For this partitioning, There is no Madelung potential and no Coulomb energy. It might be possible to carry out this procedure for an isomorphous model of the alloy, which is the only case that was considered, but even there overlapping spheres were used for which the multiple-scattering theory is not correct [30]. It becomes impossible when the polymorphous nature of the alloy is taken into account. It is necessary to find the charge distribution before the partitioning problem can be approached. The Ewald procedure is a powerful method for treating the Coulomb energies, and there is no comparable method for predicting atomic volumes.

A reason that it is possible to debate the relative merits of isomorphous CPAs versus a polymorphous CPA is that all of them work rather well for the calculation of quantities like the average charge transfer and the total energy. It has been shown that even the KKR-CPA gives

a heat of mixing that is 83% of the LDA value obtained using the LSMS [31]. The PCPA heat of mixing is 107% of the LDA value [3].

3. Averages in the CPA and PCPA

A natural concern about the PCPA is that some of the useful features of the CPA, such as a translationally invariant average Green's function and a Bloch spectral density function, will be lost in the new formalism. An acceptable average Green's function and a Bloch spectral density have been derived within the PCPA [2], but in order to achieve this it is necessary to use a site-averaging procedure that appears quite different from the ensemble average used in the coherent potential approximation [1, 32]. Some readers find the physical arguments used in reference [2] to justify the averaging procedure sufficient, but others have expressed reservations based on the observation that conclusions based on non-rigorous statistical arguments may turn out to be fallacious. The powerful mathematical theory of ergodicity is invoked here to justify the averaging procedure used in the PCPA.

In 1887 Boltzmann [33] introduced the concept of ergodicity in connection with his work on the foundations of classical statistical mechanics. Mathematicians recognized that ergodicity touches upon some highly technical aspects of measure theory, and that the argument put forward by Boltzmann cannot be true. The easiest way to see this is to note that a definition of measure that leads to a finite result for an integral over the constant-energy surface will produce the value zero for an integral on the trajectory. Birkhoff [34] is generally credited with producing the first rigorous proof of the ergodic theorem. Ergodicity has been discussed in many references [35–38], and is now included in texts on measure theory.

The rigour of these mathematical arguments will be invoked in the following, but equally important is the abstraction of the mathematical approach which is not restricted to averages over time and constant-energy surfaces. Modern ergodic theory is the study of the category of measure spaces in which the morphisms are the measure-preserving transformations. The measure space in the Boltzmann theory is the constant-energy surface, and the morphism is the group of translations in time T_t.

The simplest model of a disordered substitutional alloy is constructed by considering a Bravais lattice containing sites R_i arranged periodically in space in, e.g., the fcc or bcc structure. In a given sample, a fraction c_A of randomly chosen sites is populated with A atoms and a fraction c_B with B atoms in a specific arrangement a. The one-electron Green's function for an alloy in the arrangement a is

$$
\begin{aligned}
y_a(R_i) &= G_a(E, r, r') \\
&= \sum_{L,L'} Z_L^{a,i}(r - R_i)\tau_{L,L'}^{a,ii} Z_{L'}^{a,i}(r' - R_i) - \sum_L Z_L^{a,i}(r - R_i) J_L^{a,i}(r' - R_i)
\end{aligned}
\tag{6}
$$

where r is in the unit cell associated with the ith site $r \subset \Omega_i$ and also $r' \subset \Omega_i$. The normalizations of the wave functions $Z_L^{a,i}(r - R_i)$ and $J_L^{a,i}(r - R_i)$ are described in previous publications [32], as is the scattering path matrix τ^a.

Many properties of alloys depend primarily on the concentrations c_A and c_B, and can be obtained conveniently from the average of the Green's function over the M arrangements a:

$$
\langle y(R_i) \rangle = \frac{1}{M} \sum_{a=1}^{M} y_a(R_i).
\tag{7}
$$

As the number of atoms in the samples approaches infinity, M will become infinite. This is the kind of averaging method that is used in all of the CPA derivations [39]. The average Green's

function in the PCPA is obtained by considering a specific arrangement a, and averaging over the N sites in the sample

$$\{y_a(0)\} = \frac{1}{N} \sum_{i=1}^{N} y_a(\boldsymbol{R}_i) \qquad (8)$$

where $N \to \infty$. The question arises of whether the averages in equations (8) and (7) are the same.

In the language of ergodic theory, the set of arrangements of the atoms a is a measurable space $\mathcal{M}$. The morphism on this set is the group of translations T_R that transform the origin of the coordinates in the sample from 0 to $\boldsymbol{R}$, and is measure preserving. It is analogous to the time displacements T_t in Boltzmann's version of the ergodic theorem. The site-averaging process in equation (8) is the analogue of the time average in Boltzmann's theory, while $\langle y(\boldsymbol{R}_i) \rangle$ plays the role of the ensemble average. It is clear from their defining equations that the averaging processes commute:

$$\{\langle y(\boldsymbol{R}_i) \rangle\} = \langle \{y_a(0)\} \rangle. \qquad (9)$$

The ensemble average of the Green's functions is periodic, so it follows trivially that

$$\{\langle y(\boldsymbol{R}_i) \rangle\} = \langle y(0) \rangle. \qquad (10)$$

As M and N approach infinity, the site averages $\{y_a(0)\}$ will be the same for all arrangements a, excepting for a set of measure zero, from which it follows that

$$\langle \{y_a(0)\} \rangle = \{y(0)\}. \qquad (11)$$

The last three equations prove the ergodicity of this model:

$$\{y(0)\} = \langle y(0) \rangle \qquad (12)$$

with probability one. The condition that there is a set of elements in the ensemble for which the ergodic theorem does not hold is also true for the Boltzmann case, but the measure of such states goes to zero as $\Theta \to \infty$.

The ergodic theorem can be used in either direction. Boltzmann took the point of view that there is only one physical system, and the theorem is used to justify ensemble averages. The interpretation of molecular dynamics simulations in terms of thermodynamic quantities is based on the opposite application of the theorem. Calculations on one sufficiently large system are used to simulate the results of an ensemble average. Both ways of looking at the theorem are useful for the CPA.

The scattering path matrix τ^a that is used in the exact Green's function in equation (6) is obtained by taking the inverse of a matrix $\mathbf{M}^a$ with elements

$$M_{LL'}^{a,mn} = m_l^n \delta_{LL'} \delta_{mn} - g_{LL'}^{mn} \qquad (13)$$

where m_l^n is an element of the inverse of the t-matrix for site n, $\mathbf{t}^n$, and $g_{LL'}^{mn}$ is the matrix element of the free-electron Green's function that describes the propagation from cell m to cell n. The superscript a refers to the arrangement of the atoms, and the calculation must be iterated to obtain charge self-consistency. It is impossible to calculate the Green's function exactly for an infinitely large system, so it is useful to consider some approximations that have been made to simplify the problem.

In the isomorphous CPA [1, 32], the scattering path matrix for a site occupied by an A atom is calculated as if the atom is embedded in a lattice with the t-matrix for an effective scatterer $\mathbf{t}^c$ on every other site. Thus, $\tau^{a,ii}$ is given by the impurity formula

$$\tau^{a,ii} = [\mathbf{I} + \tau_c^{00}(\mathbf{m}^A - \mathbf{m}^c)]^{-1} \tau_c^{00} = \tau^A. \qquad (14)$$

Similarly, the scattering path matrix for a site containing a B atom is

$$\tau^{a,ii} = [\mathbf{I} + \tau_c^{00}(\mathbf{m}^B - \mathbf{m}^c)]^{-1}\tau_c^{00} = \tau^B. \tag{15}$$

These formulae have been written in terms of submatrices to eliminate the angular momentum indices. The matrices $\mathbf{m}^A$ and $\mathbf{m}^B$ are the inverses of the t-matrices for the A and B atoms. The t-matrix for the coherent potential $\mathbf{t}^c$ is obtained with a self-consistency step that is in addition to the charge self-consistency, and its inverse is $\mathbf{m}^c$. The matrix τ_c^{00} is the scattering path matrix for the periodic lattice with $\mathbf{t}^c$ on every site. It is clear that either form of averaging leads to the average Green's function

$$\{y(0)\} = \langle y(0) \rangle$$
$$= c_A \sum_{L,L'} Z_L^A(\boldsymbol{r} - \boldsymbol{R}_i)\tau_{L,L'}^A Z_{L'}^A(\boldsymbol{r}' - \boldsymbol{R}_i) + c_B \sum_{L,L'} Z_L^B(\boldsymbol{r} - \boldsymbol{R}_i)\tau_{L,L'}^B Z_{L'}^B(\boldsymbol{r}' - \boldsymbol{R}_i)$$
$$- c_A \sum_L Z_L^A(\boldsymbol{r} - \boldsymbol{R}_i)J_L^A(\boldsymbol{r}' - \boldsymbol{R}_i) - c_B \sum_L Z_L^B(\boldsymbol{r} - \boldsymbol{R}_i)J_L^B(\boldsymbol{r}' - \boldsymbol{R}_i). \tag{16}$$

This constitutes a proof by construction of the ergodic theorem for this simple model.

In the PCPA, the scattering path matrix for any site is calculated as if the atom is embedded in a lattice with the t-matrix for an effective scatterer on every other site. Thus, $\tau^{a,ii}$ is given by the impurity formula

$$\tau^{a,ii} = [\mathbf{I} + \tau_c^{00}(\mathbf{m}^{a,i} - \mathbf{m}^c)]^{-1}\tau_c^{00} \tag{17}$$

where $\mathbf{m}^{a,i}$ is the inverse of the t-matrix for the atom on site i. In the charge self-consistency step, proper account is taken of the long-range nature of the Coulomb potential, and it is for this reason that $\mathbf{m}^{a,i}$ depends on the arrangement of all the atoms in the sample a as well as the identity of the atom on the site. The self-consistency equation for the coherent potential $\mathbf{t}^c$ is slightly more complicated than for the isomorphous case. Not only the scattering path matrix but also the wave functions $Z_L^{a,i}(\boldsymbol{r} - \boldsymbol{R}_i)$ and $J_L^{a,i}(\boldsymbol{r} - \boldsymbol{R}_i)$ depend on the arrangement of the atoms.

The discussion in this section applies only to the case where the number of atoms in a sample N and the number of samples M increase without bound. An isomorphous CPA calculation can be carried out in that limit, but a PCPA calculation cannot. The ergodic theorem of equation (12) applies to the PCPA, but the ensemble average $\langle y(0) \rangle$ would require that the $\tau^{a,ii}$ be calculated taking into account the arrangement of all the atoms in every sample in the ensemble. For this reason, the site average $\{y(0)\}$ is used in the PCPA, and it is necessary to use supercells.

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