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GENERALIZED PERTURBATION METHOD EXPANSIONS OF THE TOTAL ENERGY OF AN ALLOY

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Abstract

The generalized perturbation method, commonly used in connection with the band energy contribution to the energy of a solid to approximate the total energy of an ordered configuration of an alloy is reformulated with respect to the total energy. The connection of the results derived here to those obtained based on the band energy is pointed out, and the possibility of applications of the method is discussed.

Introduction

Present-day theoretical studies of the phase stability properties of substitutional alloys are often based on two well-developed and powerful calculational disciplines: the determination of the electronic structure and the principles of equilibrium statistical thermodynamics. These two disciplines are brought together by the simple expedient of using the results of electronic structure calculations to define an alloy Hamiltonian that has the form of the Hamiltonian describing the Ising model[1], or appropriate generalizations of it. The idea, of course, is to use the powerful machinery of equilibrium thermodynamics, usually presented in an analysis of the phase stability properties of the Ising model, to study the corresponding properties of substitutionally disordered alloys.

Traditionally, the parameters that enter the Ising Hamiltonian representing an alloy have been based on the band part of the total energy of the system[2, 3, 4, 5, 6]. In the following discussion, we show how the generalized perturbation method[4, 5, 6] (GPM), one approach used to calculate the parameters of an Ising model for an alloy system, can be generalized to total energies.

In the approach described below, one first calculates the total energy of a completely random alloy using the formal and computational framework of the coherent potential approximation[7, 8, 9] (CPA), within the Green function formalism of Korringa, Kohn, and Rostoker (KKR). This formalism was introduced by KKR in the treatment of ordered materials. Its generalization to the CPA is commonly referred to as KKR-CPA[8, 9]. Once the energy of the alloy has been obtained within the KKR-CPA, a perturbation expansion is used to approximate the energy of any ordered configuration of the alloy under study.

The approach discussed below leads to the direct determination of the interactions of the Ising model and is to be contrasted with techniques[10, 11, 12] that obtain these

interactions from fitting procedures. The GPM allows one to judge the convergence properties of the interactions based on a small parameter which, in the case of binary alloys, turns out to be proportional to the difference between the scattering matrices corresponding to the atoms of the two different species in the alloy. No such parameter is evident when one uses a fitting procedure to determine these interactions.

Total Energy Expansions

We begin with an expression for the total energy of a solid, in any configuration, which can be written in the form,

$$\begin{aligned}
 E = & \int E dE \int d^3r n_v(\mathbf{r}, E) - \frac{1}{2} \int d^3r n_v(\mathbf{r}) [V_C(\mathbf{r}) + 2\mu_{xc}(\mathbf{r})] \\
 & + \int_{\Omega} n_v(\mathbf{r}) \epsilon_{xc} d^3r \\
 & + \sum_i^{\text{core}} \epsilon_i - \frac{1}{2} \int d^3r n_c(\mathbf{r}) [V_C(\mathbf{r}) + 2\mu_{xc}(\mathbf{r})] \\
 & + \int_{\Omega} n_c(\mathbf{r}) \epsilon_{xc} d^3r \\
 & - \frac{1}{2} \sum_{\nu} Z_{\nu} \left\{ \int \frac{n(\mathbf{r}) d^3r}{|\mathbf{r} - \mathbf{R}_{\nu}|} - \sum_{\alpha \neq \nu} \frac{Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\nu}|} \right\}, \quad (1)
 \end{aligned}$$

where n_v and n_c denote the valence and core contribution to the electron density, ϵ_{xc} and μ_{xc} are the exchange-correlation energy and potential, respectively, Z_{ν} is the nuclear charge at $\mathbf{R}_{\nu}$, and $V_C(\mathbf{r})$ is the electrostatic (Hartree) potential at $\mathbf{r}$,

$$V_C(\mathbf{r}) = \int \frac{n(\mathbf{r}') d^3r'}{|\mathbf{r} - \mathbf{r}'|} - \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}. \quad (2)$$

Let us isolate that part of the energy that is proportional to the valence charge and write it in the form,

$$\begin{aligned}
 E_v = & \int dE \int d^3r n_v(\mathbf{r}, E) \left\{ E - \frac{1}{2} [V_C(\mathbf{r}) + 2\mu_{xc}(\mathbf{r}) - 2\epsilon_{xc}] \right\} \\
 = & \int dE \int d^3r n_v(\mathbf{r}, E) \psi(\mathbf{r}, E). \quad (3)
 \end{aligned}$$

It can be shown[6] that, at least in the case of binary alloys, the coefficients of the Ising model are *interchange* energies and satisfy the exact relations,

$$K_n^v \equiv V_{i_1 i_2 \dots i_n}^{(n)} = \left[V_{i_1 i_2 \dots i_{n-1}}^{(n-1)} \right]_{i_n}^A - \left[V_{i_1 i_2 \dots i_{n-1}}^{(n-1)} \right]_{i_n}^B, \quad (4)$$

so that these coefficients can be determined within an iterative process beginning with the coefficient of the lowest order, $V_i^{(1)}$. For example, within a band energy approach, we have

$$V_i^{(1)} = - \int_{-\infty}^{E_F} (N_i^A(E) - N_i^B(E)) dE, \quad (5)$$

for the one-body contribution, and

$$\begin{aligned} V_{ij}^{(2)} &\equiv [V_i^{(1)}]_j^A - [V_i^{(1)}]_j^B \\ &= - \int \{ [N_{ij}^{AA}(E) - N_{ij}^{BA}(E)] \\ &\quad - [N_{ij}^{AB}(E) - N_{ij}^{BB}(E)] \} dE, \end{aligned} \quad (6)$$

for the pair interaction between sites i and j . The pair interaction is defined as the interchange energy of the one-body interaction at site i when it takes place in the neighborhood of a different site, j . In these expressions, the various integrated energies $N(E)$ are defined with respect to the indicated sites. Since these iterative relations hold in the case of total energies, all that is necessary is to start the iteration process based on a total energy expansion of $V_i^{(1)}$.

To a very good approximation, it is sufficient to work only with E_v . The core part, which is everything not included in E_v does indeed contribute to $V^{(1)}$ but, at least for monatomic systems, this term does not occur in a perturbative expansion because of the property $\sum_i \delta c_i = 0$. The core part of the energy (including terms proportional to the nuclear charge) are relatively insensitive to changes in the local environment, and because of the interchange nature of the interactions make vanishingly small contributions to them. Therefore, we proceed with the treatment of only the valence part of the energy, within the framework of the KKR-CPA. At least in this initial stage, we assume that no charge transfer takes place between cells of differing chemical composition. If the cells associated with different species are not neutral, then the results of the CPA itself can be grossly incorrect. In this case, the validity of a perturbation expansion based on an incorrect result must be questioned.

Within a multiple scattering treatment, we have

$$n_\alpha^\alpha(\mathbf{r}, E) = \sum_{LL'} Z_L^\alpha(\mathbf{r}) \hat{\tau}_{LL'}^\alpha(E) Z_{L'}^\alpha(\mathbf{r}), \quad (7)$$

where n_α^α is the local electron density at E associated with an atom of type α in the alloy, $\hat{\tau}^\alpha$ is the imaginary part of the corresponding scattering-path operator (the transition matrix)[13], and Z^α is the regular solution of the Schrödinger equation for the potential in a cell of type α which satisfies well-defined matching conditions on the surface of a sphere bounding the cell.

In the following discussion, it is convenient to work within a vector-matrix notation in angular momentum space. To this end, we define the vectors $|Z^\alpha(\mathbf{r}, E)\rangle$, whose elements are the functional $Z_L^\alpha(\mathbf{r}, E)$, and the matrix

$$\begin{aligned} \underline{f}^\alpha(E) &= \int d^3r |Z^\alpha(\mathbf{r}, E)\rangle \langle Z^\alpha(\mathbf{r}, E)| \\ &= \int d^3r \underline{f}^\alpha(\mathbf{r}, E). \end{aligned} \quad (8)$$

In terms of these matrices, we can write

$$n_\alpha^\alpha(E) = \text{Tr} \underline{f}^\alpha(E), \quad (9)$$

where

$$\underline{n}^\alpha(E) = \hat{\tau}^\alpha(E) \underline{f}^\alpha(E). \quad (10)$$

Now, in order to study disordered alloys, the energy expression must be averaged over all configurations of an ensemble at a fixed concentration. It is consistent with the spirit of the CPA and the perturbative expansions considered here to replace the disordered material with an effective medium, determined within the CPA, and to consider all sites, occupied by different chemical species, as being embedded in such a medium. We now have (with $E_v = E$),

$$\begin{aligned} E &= \text{Tr} \sum_{\alpha} c_{\alpha} \int dE \hat{\tau}^\alpha(E) \underline{f}^\alpha(\mathbf{r}, E) Y^\alpha(\mathbf{r}, E) \\ &\equiv \text{Tr} \sum_{\alpha} c_{\alpha} \int dE \hat{\tau}^\alpha(E) \underline{F}^\alpha(E). \end{aligned} \quad (11)$$

Here, $\hat{\tau}^\alpha(E)$ is the imaginary part of the scattering-path operator associated with an cell (atom) of type α embedded in the CPA medium, Z^α is the regular solution of the Schrödinger equation for the potential of such a cell, and $Y^\alpha(\mathbf{r}, E)$ is the potential, including exchange and correlation, acting on a cell of type α . For reference purposes, we note explicitly the elements of the matrix $\underline{F}^\alpha$,

$$F_{LL'}^\alpha(E) = \int d^3r Z_L^\alpha(\mathbf{r}, E) Z_{L'}^\alpha(\mathbf{r}, E) Y^\alpha(\mathbf{r}, E), \quad (12)$$

where within the CPA framework we take the "potential" $Y^\alpha(\mathbf{r})$ to depend only on the chemical occupation of cell α and to have an additive dependence on the energy. Using these definitions, we can write

$$\begin{aligned} E &= \text{Tr} \sum_{\alpha} c_{\alpha} \int dE \underline{n}^\alpha(E) \underline{f}^{\alpha-1}(E) \underline{F}^\alpha(E) \\ &= \text{Tr} \sum_{\alpha} c_{\alpha} \int dE \underline{n}^\alpha(E) \underline{G}^\alpha(E). \end{aligned} \quad (13)$$

Integration of the last expression by parts leads to the result,

$$\begin{aligned} E &= \text{Tr} \sum_{\alpha} c_{\alpha} [N^\alpha(E) G^\alpha(E)] \Big|_{-\infty}^{E_F} \\ &= \text{Tr} \sum_{\alpha} c_{\alpha} \int_{-\infty}^{E_F} N^\alpha(E) \frac{dG^\alpha(E)}{dE} dE. \end{aligned} \quad (14)$$

If, as is often done in calculations based on band energies, we neglect configurational fluctuations in the integrated term above, we obtain the following expression for the configurational energy (also called the grand potential),

$$\Omega = -\text{Tr} \sum_{\alpha} c_{\alpha} \int_{-\infty}^{E_F} N^\alpha(E) g^\alpha(E) dE. \quad (15)$$

where $\underline{g}(E) = \frac{dG(E)}{dE}$. This expression is in a particularly convenient form for the calculation of the effective cluster interactions.

From the general expression in Eq.(4), and beginning with $V^{(1)}$, which is the derivative of the last expression with respect to concentration, we find

$$V_i^{(1)} \equiv V^{(1)} = -\text{Tr} \int_{-\infty}^{E_F} \left(\underline{N}_i^A(E) \underline{g}^A(E) - \underline{N}_i^B(E) \underline{g}^B(E) \right) dE, \quad (16)$$

for the one-body contribution, and

$$\begin{aligned} V_{ij}^{(2)} &\equiv \left[V_i^{(1)} \right]_j^A - \left[V_i^{(1)} \right]_j^B \\ &= -\text{Tr} \int \left\{ \left[\underline{N}_{ij}^{AA}(E) - \underline{N}_{ij}^{AB}(E) \right] \underline{g}^A(E) \right. \\ &\quad \left. - \left[\underline{N}_{ij}^{BA}(E) - \underline{N}_{ij}^{BB}(E) \right] \underline{g}^B(E) \right\} dE. \end{aligned} \quad (17)$$

Higher ECI's can be evaluated in a fairly straightforward way.

It is clear that the last expression contains a further approximation in that it neglects the correlations between the sites in a cluster and the functions $\underline{g}^\alpha$. This approximation can be removed at non-negligible computational expense by allowing the introduction of the site-dependent diagonal matrices $\underline{g}_i^\alpha$ that would multiply each of the corresponding matrix elements in the evaluation of $\underline{N}_{i,j,\dots,k}$.

It can also be shown that the expressions in terms of integrated densities of states can be written concisely in terms of cluster matrices,

$$\underline{Q} = \left[1 - \underline{X} \hat{\underline{\tau}} \right], \quad (18)$$

which have elements in both cluster and angular momentum space. Here, $\hat{\underline{\tau}}$ is the strictly site off-diagonal part of the scattering path operator, and we have defined the "scattering matrix",

$$\underline{X}^{nm} = \left\{ (\underline{m}^n - \underline{m}) \left[1 - (\underline{m}^n - \underline{m}) \hat{\underline{\tau}} \right]^{-1} \right\}^{nm}. \quad (19)$$

In analogy with expressions based on the band energy[6], we now find

$$\begin{aligned} V_{i_1 i_2 \dots i_n}^{(n)} &= -\frac{2}{\pi} \text{Tr} \int dE \left\{ \ln \left[\left[\Pi_J \underline{Q}^{J,(\text{even}),A} \right] \left[\Pi_J \underline{Q}^{J,(\text{odd}),A} \right]^{-1} \right] \underline{g}^A(E) \right. \\ &\quad \left. - \ln \left[\left[\Pi_J \underline{Q}^{J,(\text{even}),B} \right] \left[\Pi_J \underline{Q}^{J,(\text{odd}),B} \right]^{-1} \right] \underline{g}^B(E) \right\}, \end{aligned} \quad (20)$$

where $\underline{Q}^{J,(\text{even}),A}$ is a cluster matrix for configuration J , which has an even number of B -like atoms and contains an atom of type A at the origin (center) of the cluster. It is clear from the derivation that the center of the cluster can be chosen arbitrarily without affecting the results. An analogous interpretation in terms of a B atom in the center applies to $\underline{Q}^{J,(\text{even}),B}$. The last expression yields the irreducible ECI's for a given cluster of sites within the CPA formalism.

The expression for the ECI's just derived is a perturbative expansion of the total energy, whose convergence is governed by the presence of the small parameter, $|\Delta t \hat{r}|$, as follows from the derivations[4, 5] of the GPM in connection with band energies. Therefore, the expressions defined above are similar to the GPM (and also ECM) expansions that have been derived in connection with band energies[6]. Clearly, they reduce to those expansions in a trivial way when only the band contribution to the quantity $Y^\alpha(\mathbf{r})$ is considered. Furthermore, since the potential $Y^\alpha(\mathbf{r})$ depends on the energy only through the explicit presence of the energy in an additive way, we may expect that the kinetic energy should make, in general, the largest contribution to the perturbative expansions of the energy away from the CPA values.

Discussion

As a first application of the total-energy version of the GPM presented above, we estimated the value of the first few, low-order coefficients $V^{(n)}$ by fitting to calculated total energies for selected configurations of $\text{Ni}_{0.50}\text{Pt}_{0.50}$ and $\text{Al}_{0.75}\text{PLi}_{0.25}$ alloys. In the case of the Ni-Pt alloys, the estimate of the order-disorder transition temperature improved substantially when compared with the results of the GPM used only with band energies. However, in the case of Al-Li alloys, the method predicts that the system will phase separate at low temperatures, rather than form a metastable δ' phase, as is observed experimentally. It is, of course, well known that the fitting procedure used here is unreliable and has little, if any, predictive validity. Further work, currently in progress, is aimed at a proper application of the formalism discussed above that would include the direct calculation of the various quantities that appear in the expressions for $V^{(n)}$. The results of this work will be communicated as they become available.

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