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D. de Fontaine

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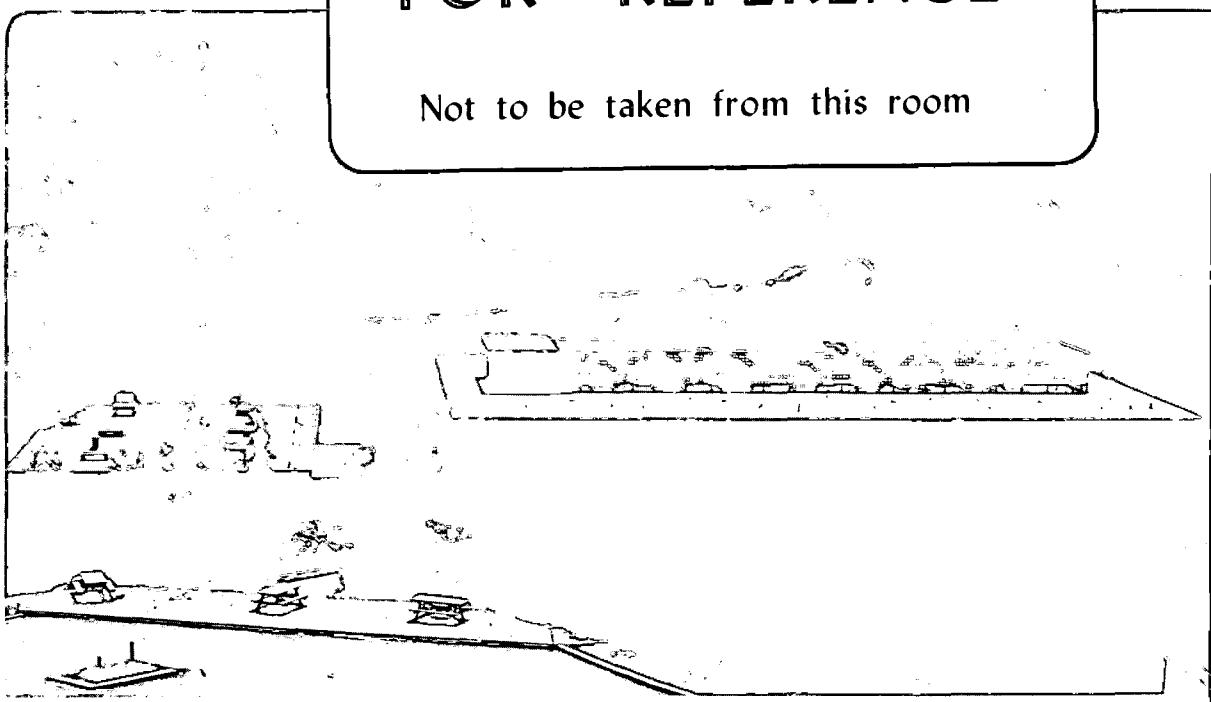

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D. de Fontaine

Department of Materials Science and Mineral Engineering
University of California

and

Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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WHY FIRST-PRINCIPLES CALCULATIONS FOR ALLOYS?

D. de FONTAINE
Department of Materials Science and Mineral Engineering, University of California, Berkeley, CA 94720, USA, and
Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

ABSTRACT. A brief non-technical overview of first-principles calculations is presented, with emphasis on prediction of phase equilibria. Merits and drawbacks of various methods are briefly discussed.

1. Introduction

What are *first-principles calculations* and what can be done with them? In view of the importance of this topic and of the misunderstandings which it has generated, it may be useful to try to answer these questions at least qualitatively. Such is the purpose of this brief paper. The literature on the subject is now quite vast, so that no attempt will be made here to review the field. Bibliography is cited only sparingly.

Ultimately all materials problems are quantum mechanical in nature. Does that mean, however, that we should try to improve the ductility of, say, high-temperature alloys by solving the Schrödinger (or Dirac) equation? Surely not. Should we construct a *supercell* with a grain boundary in it, and let a dislocation run through it while we compute all energies by electronic band structure calculations? Such a huge "brute force" undertaking is quite unnecessary, besides being unrealistic.

Rather, we should continue to use classical, macroscopic, continuum models which have been around a long time and which are currently taught in Materials Science and Physics Departments: elasticity, plasticity, dislocation theory, fracture mechanics, bulk and surface thermodynamics, and so on. In the past, these classical theories have not been used to full advantage because, very often, materials parameters required "to make the equations go" were unavailable. What first-principles calculations can now provide, however, are values for these elusive parameters. In other words, quantum mechanical calculations can generate the required *data bases*, so that, for the first time in the relatively young history of Materials Science, theory can become truly predictive, with first-principles calculations serving to establish a continuous computational path from purely atomic phenomena all the way to practical problems concerning, say, mechanical properties.

By *first-principles* or *ab initio* calculations we mean, in the present context, more than just calculating cohesive energies of crystals knowing the atomic numbers and locations of atoms in the unit cell; we also mean calculating entropies, hence free energies. Hence, good statistical mechanical models, which are also tractable, must be available, along with interaction energies which determine the system's thermodynamics. It follows that such *ab initio* calculations require the solution of both quantum and statistical mechanical problems. Moreover, computations must be carried out with a high degree of accuracy since important parameters generally result from small differences of large numbers.

Some of the electronic energy calculation techniques currently in use for perfect crystals at absolute zero of temperature will be briefly described in Section 2, then the extension to disordered systems will be discussed in Section 3. Applications to phase diagrams will be mentioned in Section 4. For reviews of the subject matter treated here the interested reader may consult Refs. [1]-[3].

2. Perfect Crystals at Absolute Zero

Let the term "perfect crystal" denote a crystalline stoichiometric compound free from imperfections or, of course, an elemental crystal. The problem is to calculate the *cohesive energy* of the compound in a given crystal structure, i.e., the difference in energy between the crystalline aggregate and the isolated atoms. It is necessary to solve the Schrödinger (or Dirac) equation for the electronic states of each free atom and for the periodic crystalline structure. As by-products, one obtains electronic densities of state and, when the wave functions are calculated, the local electron density in the unit cell.

The problem is impossible to solve exactly, since all electrons interact dynamically with themselves and with atomic nuclei, some 10^{22} in number. Hence, drastic simplifications are required. Since the nuclei are so much more massive than the electrons, one first assumes that the nuclei are stationary and occupy fixed lattice positions. By this decoupling procedure, nuclei dynamics can be handled subsequently at non-zero temperatures by lattice dynamics methods.

The remaining problem is still very difficult: that of electrons interacting with the field of fixed nuclei and with all other electrons. Here, one generally makes the important one-electron approximation, i.e., one solves self-consistently for a single electron moving in the effective potential field of the nuclei and the charge density of all other electrons. Various methods have been proposed for carrying out these self-consistent calculations, the most frequently used being the local density functional method (LDF) [4] which has made first-principles calculations feasible on fast computers.

The time-independent Schrödinger equation applied to solids reduces to an extremely large eigenvalue problem which can be solved in principle by two types of mathematical techniques: variational methods or Green's function methods. In either case, wave functions may be expanded in orthonormal sets of functions, the choice of which depends on computational convenience but also on the nature of the simplified potential adopted.

Atomic potentials have a spherically symmetric $1/r$ dependence near the nucleus but lose that symmetry nearer to the Wigner-Seitz cell boundaries. One simplification consists of replacing the true potential in each WS cell by a central spherically symmetric one terminating, near cell edges, in a perfectly flat potential. Such is the so-called muffin-tin (MT) potential. This potential is adopted by various computational methods which then differ from each other by the choice of basis functions: APW (augmented plane waves), ASW (augmented spherical waves), and KKR (Korringa-Kohn-Rostoker, a "multiple scattering" method). A linearized version of the latter, i.e., one which, by expansions about fixed energy values, converts complicated determinental equations into simpler secular equations, goes by the name of LMTO (linear muffin-tin orbital). A further simplification is possible, that which consists of eliminating the "interstitial" region between MT spheres altogether by allowing them to overlap. Such is the atomic sphere approximation. The resulting method, the LMTO-ASA, is extremely efficient but works best for close-packed structures. Other methods can be "linearized" as well, resulting in the LAPW method, for example.

The trouble with the spherically symmetric muffin-tin potential is that departure from simple local symmetry cannot be handled properly. Hence, in order to handle, say, c/a relaxation in tetragonal unit cells, or distortions required to compute elastic constants, full (F) potentials must be retained in the formalism. Corresponding electronic structure methods go by the acronym FLAPW, FLMTO.

For molecules, one often uses as basis functions the atomic orbitals themselves. Wave functions are then built up by linear combinations of atomic orbitals (LCAO). That method can of course be used for (infinite) periodic structures as well, but the matrix elements of the Hamiltonian are very difficult to compute *ab initio* in this basis. It is then customary to obtain these elements from fits to the band structure or as derived from the LMTO [5]. The ingredients of matrix elements are then treated as parameters of the model and electronic self-consistency is handled in an approximate manner. One then has the very convenient, physically meaningful, but sometimes computationally unreliable tight-binding approximation (TB), which nevertheless works rather well for transition metals. Finally, let us mention pseudopotential techniques, which are particularly well suited to covalently bonded structures [6].

Computer codes required to perform the calculations are of such complexity that non-initiates are well advised not to attempt to write their own versions. Fortunately, ready-made, quasi "black box" LMTO-ASA, APW, and ASW codes are available and, to a lesser degree, KKR and FLMTO codes. Tight-binding codes are simple enough to generate, but Cambridge University puts out a nice package which includes the clever recursion algorithm for calculating electronic densities of state for disordered systems [7]. Still, as for all sophisticated techniques, one must know the principles of the method quite well in order to use the tool to full advantage. To borrow an analogy familiar to all materials scientists, it is not necessary to build an electron microscope oneself, but one must know the principles of operation very thoroughly in order to operate the instrument effectively. Also, the more powerful the instrument, the longer must be the learning stage for successful utilization.

It is also true that "you get what you pay for": high reliability and accuracy require elaborate codes with long running times. As a general rule, for modest-size problems, tight binding can be run on a PC, LMTO-ASA on a work station, and APW, KKR, particularly full potential codes, on a supercomputer. Of course, CPU times depend critically on the size of the problem: if the unit cell contains N atoms, the running time will be proportional to N^3. That is a very serious limitation which prevents certain very interesting problems from being tackled at all, at present.

3. Disordered Systems

3.1 DEFECTS

The simplest type of configurational disorder is the isolated point defect, a vacant lattice site, for example. The introduction of a defect breaks translational symmetry so that the great simplification offered by application of the Bloch Theorem, valid for periodic structure, can no longer be used. To restore translational symmetry, what is usually done is to set up a periodic lattice of supercells, each one containing identical copies of the defect configuration considered. Care must be taken, however, to insure that the lattice parameter of the supercell array be significantly larger than the linear dimensions of the defect(s) to be calculated. If the defects are (relatively) too close together in supercell space, then the calculation yields not just the self-energy of the defects that one wishes to calculate, but also the interaction energies which are an artifact of the repeating nature of the

the repeating nature of the defects in their supercells. It is clear, therefore, that the N^3 computational rule referred to above, where now N is the number of atoms in the supercell, severely limits the application of the method to very simple defect structures.

Next in order of complexity are extended defects such as dislocations, surfaces, interfaces, antiphase boundaries, etc. Again, the supercell technique may be used, but what is gained in accuracy by performing detailed first-principles calculations is often lost by the necessity of solving rather artificial problems. Rather than carrying out brute force calculations, it is usually preferable to use semi-empirical potentials, obtained from "embedded atom" techniques [8], and to model actual atomic configurations, relaxation included, by molecular dynamics. Gross features of extended defect structures and estimates of formation energies can be obtained by these methods, which, however, appear not to be sufficiently accurate at present to predict the thermodynamics of ordered or partially ordered (or disordered) structures. This problem is taken up in the next section. A very promising method of calculating cluster energies for use in extended defect problems has been introduced recently by Pettifor [9]. Green's functions techniques are also being developed for isolated defects in essentially infinite solids.

3.2 DISORDERED ALLOYS

As a first step, consider concentrated alloys in a state of complete disorder. Here, the supercell idea is not applicable: the unit cell is the whole crystal itself. The term "complete disorder" means a distribution of, say, A and B atoms, of specified average concentration c, where atomic site occupations are completely uncorrelated. With that understanding, a method for calculating average electronic structures and cohesive energies naturally suggests itself: calculate the required properties of a particular configuration in a given crystalline region, repeat the calculation for all configurations which conserve the chosen average concentration, and take averages of the results. Even in a small region and for a small number of sample configurations, such a computation requires prohibitively long computational times, unless a simple electronic structure approach is used, such as the tight binding method. This procedure, labeled DCA (direct configurational averaging), has been used with success for certain transition metal alloys [10].

If more elaborate and accurate electronically self-consistent methods are required, configurational averaging must be replaced by a technique which, by creating as it were identical "average atoms," restores translational symmetry to disordered systems. That method, known as the "coherent potential approximation" (CPA) [11], defines an average atomic potential (in a binary alloy, say) by requiring that the replacement of it, on the average, by an A or a B potential causes no additional electronic scattering. The average potential is thus determined self-consistently, usually in fewer iterations (electronic self-consistency not included) than are required for configurational averaging. The CPA is a mean field technique, unlike the DCA, since the properties of an (artificial) average structure are computed rather than the average of properties. Nevertheless, the CPA has given very reliable results, say, for the density of states of completely disordered systems [12]. Let us note, finally, that the CPA relies on the calculation of an average Green's function, hence must be used in conjunction with the tight binding method, the KKR, or, very recently, with the LMTO-ASA.

3.3 PARTIAL ORDER

Perfectly ordered or completely disordered structures at absolute zero cannot describe real alloys, and cannot deal with the complexities of phase stability as a function of temperature, for example.

Then the properties of phases, stable or metastable, must be calculated as a function of temperature and concentration c (or "chemical field" μ, a difference of chemical potentials). Better yet, what is sought is a way of determining properties as a function of alloy configuration. In what follows, it is understood that "disorder" designates atomic (A, B, ...) disorder on the sites of a *given lattice*. Complete order then produces *superstructures* of the given lattice (usually fcc or bcc).

A general and rigorous method exists for expanding in a set of basis functions any alloy property which depends on configuration:

$$f(\sigma) = \sum_{\alpha} f_{\alpha} \varphi_{\alpha}(\sigma) \quad . \tag{1}$$

In this equation, first derived by Sanchez, Ducastelle and Gratias [13], σ denotes an arbitrary crystal configuration (location of A and B atoms on lattice sites, in the binary A-B case), $\varphi_{\alpha}(\sigma)$ are *cluster functions* which may be chosen to form an orthonormal set, f_{α} are the coefficients of the expansion, and the index α denotes clusters of lattice sites: point, pairs, triplets, quadruplets, etc. Energies (formation, ordering, ...), elastic moduli and other properties may be thus expanded. What is required in macroscopic systems is the expectation values of the properties $f(\sigma)$, averaged over configurations:

$$< f > = \sum_{\alpha} f_{\alpha} \xi_{\alpha} \tag{2}$$

where, at least for binary systems, the ξ_{α} are correlation functions: point (average concentration), pair, triplet, ..., in general, multisite correlation functions. The expansion has been shown to be valid for both concentration-dependent and -independent coefficients f_{α} [14].

Eq. (2) shows very clearly how the statistical and quantum mechanical calculations are decoupled, in some sense: the f_{α} coefficients are obtained from electronic band structure calculations at absolute zero, the ξ_{α} correlations are obtained by minimizing a free energy functional at the temperatures and average concentrations of interest. The cluster variation method (CVM) [15] free energy functional is most commonly used as it is naturally expressed as a function of multisite correlation functions, the ξ_{α}, and, when used with large enough clusters, has proved to be highly accurate and reliable.

The problem, of course, is to calculate the coefficients f_{α}. As was seen in Section 2, quantum mechanical techniques exist for calculating energies of perfectly ordered or completely disordered crystals for which the considerable simplification of translational symmetry is available, either because it is naturally present in stoichiometric compounds, or because it is imposed by the CPA on disordered crystals. There are thus basically two methods for obtaining the f_{α} expansion coefficients: that based on perfect order calculations, and those based on complete disorder.

The former, which may be called the "structure inversion method," was first used by Connolly and Williams [16] and often goes by the names of these two authors: one decides which clusters α are going to contribute importantly, say, to the energies of partially ordered structures. Then a number of ordered superstructures are selected, at least equal in number to the non-equivalent clusters considered, and total energy *ab initio* calculations are performed on each superstructure. Since the ξ_{α} correlations can be calculated exactly for perfect superstructures, hence are considered "known," Eqs. (2), written for all structures calculated, form a linear system in the f_{α} unknown,

which can be solved by matrix inversion or least squares optimization. This method has many advantages since it is generally simpler and more accurate to compute properties of perfect crystals than of disordered ones, and since more flexibility is available in the choice of band structure computational techniques. All of the electronic structure methods mentioned in Section 2, and more, may be used. The disadvantage of the inversion method is that the resulting values of the f_α coefficients depend to some extent on the choice of superstructures. This undesirable feature is attenuated by considering a large enough set of structures to calculate [17].

The other methods, based on disorder, consist in calculating the f_α directly as responses of the disordered system to the perturbation caused by the corresponding cluster function φ_α. If the perturbing function is a harmonic concentration wave in the CPA medium, we have the $S^{(2)}$ method of Györffy and Stocks [18] or, equivalently, the original k-space generalized perturbation method (GPM) of Ducastelle and Gautier [19]. Today, the real-space GPM method is generally used [20], or the embedded cluster method (ECM) [21], both consisting of cluster perturbations of the single-site CPA medium. As mentioned above, the multiple scattering formalism must be used (KKR) or, in simplified form, the tight binding approximation. In this way, each cluster coefficient f_α is computed independently of the others and the calculation is pursued until the f_α for large clusters become very small. The series (1) or (2) are known to converge, but no general theoretical convergence criterion is available at present. The KKR-CPA is unfortunately a highly computationally-intensive method and at present rather unwieldy.

An alternative method has already been mentioned: the method of direct configurational averaging (DCA). Small clusters are embedded in a medium which is averaged by repeated choices of random configurations, that of the embedded cluster remaining fixed. This technique, which does not rely on the mean field approximation, is very efficient when applied in the tight binding formalism used in conjunction with the so-called "orbital peeling algorithm" [22]. The disadvantage of this technique is that only simplified band structure methods, such as the TB, have been used up to now, hence are not applicable to all alloy systems.

4. Phase Diagram Calculations

There are several reasons for wishing to calculate *ab initio* temperature-composition phase diagrams. First of all, if the phase diagram is not known empirically, it is of course useful to determine theoretically what the diagram may look like, even approximately. Such was the case for the oxygen-ordering $YBa_2Cu_3O_x$ phase diagram: the diagram was calculated from first principles [23] and, subsequently, experimental phase transition points were found to fall almost perfectly on the calculated phase boundaries [24]. Secondly, even when, as is usually the case, binary phase diagrams have been empirically determined, it is useful to perform the calculations for the following reasons: if calculated and experimentally determined phase diagrams agree reasonably well, it means that the calculations, which are very complex ones, are accurate and that the methods are sound. It is found indeed that the nature of the phases present at equilibrium and the location of phase boundaries depend critically on the accuracy of the calculations. Hence, the phase diagram is an extremely sensitive test of the computations. Also, calculations give information not only about equilibrium but also about metastable phases, which can be of considerable interest to alloy designers. Finally, and perhaps most importantly, if one can calculate a phase diagram, one has at one's disposal all quantitative information concerning formation energies, entropies, free energies, states of order, lattice parameters, elastic moduli, etc., of stable and metastable structures in all concentration and temperature ranges.

The calculations proceed roughly as follows: first, the appropriate lattices are selected, i.e., those which are expected to be parent to the terminal solutions and superstructures found in the system. Then the f_α *for each lattice* are determined by one of the methods alluded to above. With these sets of values, one can then perform, for each lattice, a ground state analysis along the lines described elsewhere in these workshop proceedings [25]. In some cases, it is possible to predict truly *ab initio* which will be the stable superstructures, without actually guessing at a number of competing structures and calculating, *a posteriori*, which are the ones with lowest energy at absolute zero.

Statistical mechanical methods (CVM, Monte Carlo simulation) are then used to determine free energies as a function of temperature and chemical field for the various lattices and their relevant superstructures. Common tangents are constructed in the usual way and phase boundaries plotted. Up to now, only crystalline phases can be handled in this first-principles way. The liquid can be included by means of a fitted free energy curve.

The degree of success and degree of difficulty encountered in this type of undertaking depend critically on the system envisaged. For example, in the Al-Li case [26], relevant intermetallic compounds were almost all superstructures of fcc and bcc lattices, and were stabilized by effective cluster interactions (ECI, f_α coefficients pertaining to configurational energy) limited to first neighbor coordination shell for fcc and first and second for bcc. Hence, small clusters could be used in the CVM free energy functional, and only a few structures needed to be calculated for the Connolly and Williams inversion. The resulting phase diagram and calculated parameters, such as lattice parameter, formation energies, and bulk moduli agreed closely with experimental values [26].

For Al-Ti, the situation is entirely different. Superstructures of fcc, bcc and also hcp are expected, and some of these structures can only be stabilized by fairly distant effective interactions [27]. Moreover, tetragonal distortions of non-cubic equilibrium phases are important and have to be taken into account in the perfect-structure calculations, which means that the structures must be "relaxed" not only with respect to atomic volume (or lattice parameter a), but also with respect to c/a and even b/a ratios and unit cell angles. That, in turn, means that only full potential codes may be used, turning the complete set of calculations into a very elaborate undertaking indeed. In addition, local elastic relaxations are expected to be important in the disordered states as well, and vibrational entropy will have to be included to stabilize bcc over hcp on the Ti-rich side of the phase diagram. Neither of these *displacive* forms of disorder has received adequate theoretical formulations. Needless to say, no one has yet "tamed" the Al-Ti system computationally, although it is technologically a highly relevant one.

Often, several different techniques must be brought to bear on the problem. For example, in a very recent work [28], FLAPW was used to calculate very precisely the cohesive energies of pure fcc and bcc Cu and Zn, the KKR-CPA-GPM combination was used to obtain the energies of complete fcc and bcc disorder in Cu-Zn and the effective cluster interactions as a function of concentration for both lattices, and an empirical Debye correction was used to stabilize bcc Cu at high temperature (above the melting point). In that way, the solid-state (no liquid) Cu-rich portion of the Cu-Zn phase diagram was calculated, including fcc and bcc superstructures, some inaccessible in practice due to sluggish kinetics at low temperatures. Predictions about diffuse scattering in α-brass were made by the equivalent of the $S^{(2)}$ method.

5. Conclusion

The full dynamical problem of interacting electrons and nuclei, which the Car-Parrinello method [29] attempts to tackle head-on, is rendered tractable by successive decoupling procedures: electronic motion is decoupled from nuclear (or ionic) motion by the Born-Oppenheimer approximation, and electronic structure calculations at absolute zero are decoupled from equilibrium configurational calculations by performing cluster expansions, Eqs. (1) or (2). The decoupling of vibrational and configurational entropy contributions then allows phase equilibrium determination on a given lattice to be handled as an Ising model problem [30].

Although much remains to be done, the various methods which have been developed to perform the required calculations have produced very encouraging results. It is therefore hoped that, in the near future, a true First-Principles Thermodynamics of Alloys will become available.

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