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# Gradient equivalent crystal theory

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## Abstract

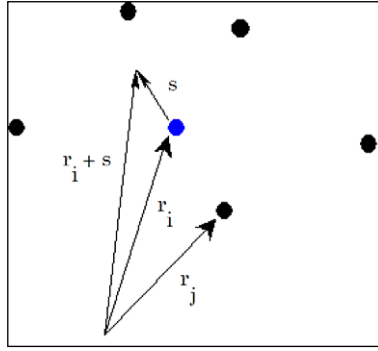
This paper presents an extension of the formalism of equivalent crystal theory (ECT) by introducing an electron density gradient term so that the total model density becomes a more accurate representation of the real local density. Specifically, we allow for the electron density around a lattice site to have directionality, in addition to an average value, as assumed in ECT. We propose that an atom senses its neighbouring density as a weighted sum—the weights given by the its own electronic probability. As a benchmark, the method is used to compute vacancy migration energy curves of iron. These energies are in good agreement with previously published results.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Equivalent crystal theory (ECT) [1] provides a framework for calculating the configurational energies of atomic systems. It has been successful in predicting the formation energies of bulk defects. Bozzolo, Ferrante and Smith (BFS) have extended it to multicomponent metals, and have successfully used it to predict the ground state structures and surface properties of various alloys [2, 3]. Currently, Bozzolo *et al* [3] have abandoned experimental input completely, relying entirely on *ab initio* results to fix the parameters of the theory. This has freed the theory from requiring parameters that are not available or do not exist in nature, e.g. bcc aluminium.

The basic idea of the original ECT rests on the fact that the total ground state energy of a quantum system is a functional of the electron density [4] as specified in density functional theory (DFT). ECT requires that, at the atomic site under consideration, the density be the same for both the real lattice with defects and an equivalent, defect-free lattice, that provides a value for an equivalent lattice parameter  $a_{\text{eq}}$  at that site for an expanded or contracted perfect crystal of that material. This is formally based on a perturbation approach where the difference in energy of a crystal with defects and an expanded or contracted perfect crystal whose energy dependence is given by the UBER (the universal binding energy relation) is minimized [5]. The UBER provides binding energy as a function of lattice parameter for the perfect, i.e. defect-free, lattice. In this work, we generalize ECT without changing its original flavour, that is, by



**Figure 1.** The black spheres represent the position of the neighbouring atoms. The point located at  $\vec{r}_i$  is the central atom under consideration. The vector  $\vec{s}$  labels positions around the central atom.

keeping the assumption that the electron density must remain the same for both the real and the equivalent crystal. However, here we extend it to include non-local effects by requiring that both the real and the equivalent crystal densities be the same not only at the atomic site under consideration, but also in a neighbourhood around that point.

In ECT, the atomic contribution to the total energy of a real crystal is calculated by evaluating the UBER at the local density in which the atom is embedded. In the original formalism, the density of neighbouring atoms is evaluated at the centre of the atom of interest, making the energy functional  $U[\rho(\vec{r})]$  a function  $U[\rho_0]$ , with density  $\rho_0 = \rho(0)$ .

Since in DFT the energy depends on the global form of the density, not only on its value at the origin; here we take that global form into consideration but preserve the usefulness of the ECT framework, particularly its use of the UBER. We will refer to this new approach as gradient equivalent crystal theory (GECT).

In section 2, we present GECT and its general implementations. In section 3, as a benchmark, we apply the method to the specific case of the vacancy migration energy in iron. Finally, section 4 presents conclusions.

## 2. Gradient equivalent crystal theory

We begin by writing the local density, around an atom of interest, as a multipolar expansion. Next, we will obtain the expression for the energy including the monopole and the dipole terms. The monopole term, we will show, corresponds to ECT.

In ECT it is necessary to evaluate the total electron density due to the presence of neighbouring atoms (figure 1). Call this density  $\rho(\vec{s})$ . This quantity does not include the atomic density produced by the atom  $i$  itself, only the density in which it is embedded. The ECT atomic densities are given by

$$f(\vec{R}) = BR^p e^{-\alpha R}, \quad (1)$$

where  $\vec{R}$  is the position vector from the centre of the atomic electronic distribution.  $B$  is a normalization constant, and  $p$  and  $\alpha$  are material-dependent constants tabulated in [1].

We proceed in two steps. First we expand the density  $\rho(\vec{s})$  in the neighbourhood of site  $i$  ( $\vec{s} \approx 0$ ) up to the dipole term. Then we expand the energy, taking the dipole term into account.

At site  $i$ , the density from neighbours is

$$\rho_i(\vec{s}) = \sum_j f(\vec{r}_i - \vec{r}_j + \vec{s}). \quad (2)$$

For small  $\vec{s}$ ,

$$\rho_i(\vec{s}) \approx \sum_j f(\vec{r}_i - \vec{r}_j) + \vec{s} \cdot \sum_j \nabla f(\vec{r}_i - \vec{r}_j) \tag{3}$$

where

$$\sum_j f(\vec{r}_i - \vec{r}_j) = \rho_0 \tag{4}$$

as defined above, and

$$\Delta\rho_0^+ \equiv \frac{\int_{\text{UHS}} f(\vec{s}) [\vec{s} \cdot \sum_j \nabla f(\vec{r}_i - \vec{r}_j)] d\vec{s}}{\int_{\text{UHS}} f(\vec{s}) d\vec{s}} \tag{5}$$

where UHS stands for upper half space. This is the neighbouring density increment weighted by the local atomic density in the direction of the gradient. The idea behind this definition is that the more the local charge is at a given location, the stronger the atom will sense the presence of the atoms around it. In the original ECT formulation, it was implicitly assumed that the local density was a Dirac delta function, thus effectively identifying  $\rho_i(\vec{s})$  with  $\rho_0$ .

A similar definition provides

$$\Delta\rho_0^- = -\Delta\rho_0^+$$

that is the decrease in charge in the direction opposite to the gradient.

It is convenient to express equation (5) explicitly, in spherical coordinates,

$$\Delta\rho_0 = \frac{\int (s^p e^{-\alpha s}) [s |\sum_j \nabla f(\vec{r}_i - \vec{r}_j)| \cos \theta] (s^2 \sin \theta ds d\theta d\varphi)}{\int (s^p e^{-\alpha s}) (s^2 \sin \theta ds d\theta d\varphi)} \tag{6}$$

where we use standard notation,  $\theta$  being the angle between  $\vec{s}$  and  $\nabla f$ .

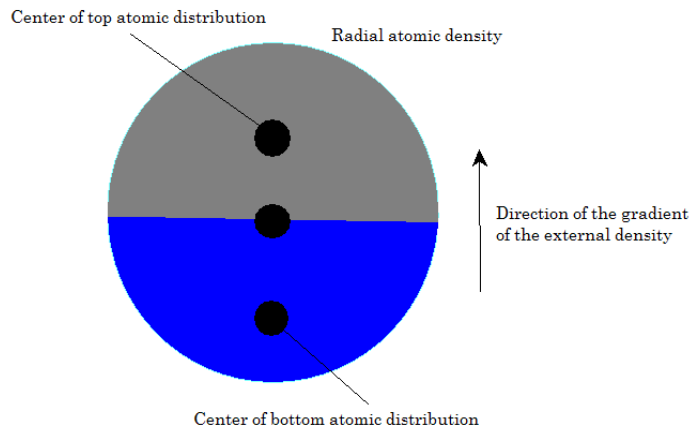
Then,

$$\Delta\rho_0 = \frac{p+3}{2\alpha} \left| \sum_j \nabla f(\vec{r}_i - \vec{r}_j) \right|. \tag{7}$$

Using the explicit expression for  $f(\vec{R})$  in equation (1),

$$\Delta\rho_0 = \frac{p+3}{2\alpha} \left| \sum_j \left( \frac{p}{|\vec{r}_i - \vec{r}_j|} - \alpha \right) f(\vec{r}_i - \vec{r}_j) \frac{(\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} \right|. \tag{8}$$

Next we develop the equations to calculate the contribution to the total energy from the central atom. Figure 2 shows a cartoon of a spherically symmetric atomic electron density distribution around the central nucleus. The gradient of the external density gradient at that point is indicated with an arrow in the figure. Along that direction we consider two points, the centres of the atomic density distributions in the upstream and downstream hemispheres. At the centre point upstream we measure a density  $\rho_0 + \Delta\rho_0$ , where for simplicity in notation we have dropped the '+' superscript. Similarly, at the centre point downstream we measure a density  $\rho_0 - \Delta\rho_0$ . According to equation (5), when the external gradient vanishes at the centre, the two charges are the same. This is what happens, for example, when the atoms are arranged in a perfect crystal pattern. In real systems with defects, there might be an imbalance of atoms that creates a non-vanishing gradient. In this case, we offset the centre to sense the external charge distribution and we find that it is slightly larger in one direction than in the opposite. Then, the upstream region of the central atom believes it is embedded in a slightly larger density than the downstream region. Thus, the upstream region senses that it belongs to an equivalent crystal with nearest neighbour distance  $R_{\text{eq}}^+$ , while the downstream senses that it to belong to  $R_{\text{eq}}^-$ .



**Figure 2.** The sphere represents a radial atomic density distribution. The top region corresponds to half that distribution in the direction of the external gradient. The centre of that distribution is the black dot on top. Likewise for the bottom region corresponding to points upstream the external gradient.

We set up the GECT equations connecting the densities of the real material and the equivalent crystal, upstream and downstream respectively:

$$N(R_{\text{eq}}^+)^p e^{-\alpha R_{\text{eq}}^+} = \rho_0 + \Delta\rho_0 \quad (9a)$$

$$N(R_{\text{eq}}^-)^p e^{-\alpha R_{\text{eq}}^-} = \rho_0 - \Delta\rho_0 \quad (9b)$$

where  $\rho_0$  and  $\Delta\rho_0$  are given explicitly in equations (4) and (8).

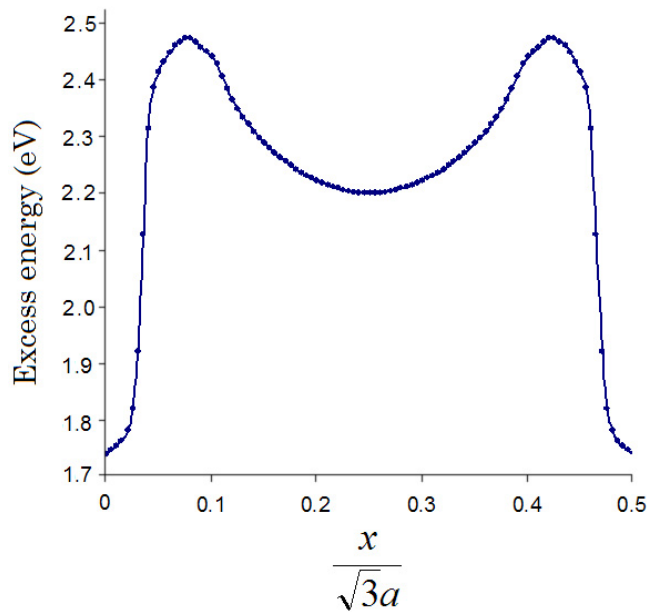
We now write the contribution to the total energy from the central atom as the half sum of the upstream and downstream contributions:

$$\varepsilon = \frac{1}{2}[U(R_{\text{eq}}^+) + U(R_{\text{eq}}^-)] \quad (10)$$

where  $U(R_{\text{eq}})$  is the UBER from [1].

### 3. Benchmark of the method: vacancy migration energy

In this section, we apply the general method developed in the previous section to calculate the vacancy migration energy curve for iron. Consider a standard cubic cell of bcc iron. Suppose that a vacancy exists at one of the corners—call that corner the origin. That configuration has an excess energy as compared with the perfect crystal, equal to the vacancy formation energy. Next, let the atom at the centre of the cube move toward the origin. As it moves, the excess energy changes. A plot of this excess energy as a function of the central atom position is the *vacancy energy curve*. We show it in figure 3. With the central atom in its initial position, at the centre of the cube, we recover the vacancy energy formation energy 1.7 eV. As the atom now moves away from the central point, the excess energy increases because of decreasing local neighbouring charge density. There is a metastable point at 1/4 the diagonal length. This is to be expected since, at that location, the central atom senses exactly the same electronic neighbourhood toward the origin or toward the centre of the cube. From the graph we also obtain a migration energy for of  $2.48 - 1.73 = 0.75$  eV, although at low temperatures a tunnelling mechanism may be dominant with a migration energy of  $2.20 - 1.73 = 0.47$  eV. These values are in agreement with calculations based on iron interatomic potentials [6].



**Figure 3.** Energy of the system as a function of the position  $x$  of an atom next to a vacancy. The full length of the horizontal axis correspond to half a diagonal of the standard cell.

#### 4. Conclusions

This paper introduced GECT, whose main features are the introduction of a gradient term in the density enabling the possibility of anisotropic deformations of the equivalent lattice. We obtained the vacancy energy curve, which provides correct values for the vacancy energy formation energy and vacancy migration energy. The new results are interesting because no fitting parameters, other than those provided by ECT, were used. This work opens the question as to whether a general multipolar expansion would in fact be the best procedure to follow within the framework of ECT. We believe that the answer to this question is positive, but further work is required to validate this hypothesis.

#### Acknowledgment

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