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A Multisite Interaction Expansion of the Total Energy in Metals

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Abstract

The local-density approximation provides a proper setting for the decomposition of the total energy into many-body (many-atom) contributions. Multiple scattering theory in turn provides a convenient framework for carrying out this process. We illustrate this concept with calculations on a linear chain of atoms in bulk copper.

1 Introduction

In studies of the structural stability of materials, it is often useful to write the total energy of an arrangement of atoms as a sum of irreducible n -body contributions

$$E = \sum_i E_i^{(1)} + \frac{1}{2} \sum'_{i,j} E_{ij}^{(2)} + \frac{1}{3!} \sum'_{i,j,k} E_{ijk}^{(3)} + \cdots \quad (1)$$

The prime on a summation denotes the omission of terms for which two indices are the same. The irreducible n -body interatomic potential $E_{i_1 \dots i_n}^{(n)}$ is defined so that it contain no contributions from clusters of lower order.

Many simulations are performed using potentials fit to experimental data.[1] However, potentials derived from first principles are desirable, since they may elucidate the mechanisms underlying structural stability. A number of attempts to derive first-principles interatomic potentials[2–6] have been made to date. In this paper we propose a derivation based on multiple-scattering theory (MST). MST offers a number of advantages for this purpose: (1) The scattering-path operator formalism[7] *automatically* sums all scattering diagrams contributing to a particular many-atom term; (2) one may obtain system-specific potentials for local and extended defects, thus eliminating

transferability questions; and (3) one can treat substitutionally-disordered alloys within the framework of the coherent-potential approximation and the generalized perturbation method.[8]

2 Irreducible Decomposition of the Total Energy

The total energy of a solid may be separated into core and valence contributions. The core part is relatively insensitive to local changes in the environment, so we focus on the valence contribution:

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

where $V_C(\mathbf{r})$ is the electrostatic (Hartree) potential at $\mathbf{r}$,

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

n_v denotes the valence contribution to the electron density, ϵ_{xc} and μ_{xc} are the exchange-correlation energy and potential, respectively, and Z_{α} is the nuclear charge at $\mathbf{R}_{\alpha}$. (We are assuming that the electronic-structure calculation has been carried out to self-consistency, i.e. $V_{in} = V_{out}$).

We shall illustrate the irreducible decomposition of the energy with the simple case of an elemental solid with monatomic unit cells. Let t_i be the scattering matrix associated with the i th atom, and Z be the corresponding regular solution of the Schrödinger equation. Then we may write the first-order contribution to the valence density, $(n_v)^1$, as

$$(n_v)_i^1 = -\frac{1}{\pi} \text{Im} \langle Z | t_i | Z \rangle. \quad (4)$$

When inserted into Eq. 2, this yields the reducible single-atom energy E_i^1 . For two atoms, we may write the second-order contribution to the valence density as

$$(n_v)_{ij}^2 = -\frac{1}{\pi} \text{Im} \langle Z | \begin{pmatrix} t_i^{-1} & -G_{ij} \\ -G_{ji} & t_j^{-1} \end{pmatrix}^{(-1)} | Z \rangle, \quad (5)$$

where G_{ij} is the propagator (structure constant) connecting site i to site j . With this expression inserted for n_v in Eq. 2, we obtain the reducible two-body

contribution, E_{ij}^2 . We define the irreducible two-body energy of the pair by subtracting all the irreducible contributions from subclusters of lower order:

$$\begin{aligned} E_{ij}^{(2)} &= E_{ij}^2 - E_i^{(1)} - E_j^{(1)} \\ &= E_{ij}^2 - E_i^1 - E_j^1. \end{aligned} \quad (6)$$

Similarly,

$$\begin{aligned} E_{ijk}^{(3)} &= E_{ijk}^3 - (E_{ij}^{(2)} + E_{jk}^{(2)} + E_{ki}^{(2)}) - (E_i^{(1)} + E_j^{(1)} + E_k^{(1)}) \\ &= E_{ijk}^3 - E_{ij}^2 - E_{jk}^2 - E_{ki}^2 + E_i^1 + E_j^1 + E_k^1. \end{aligned} \quad (7)$$

This procedure is easily extended to obtain the irreducible n -body energy associated with a subcluster of n atoms embedded in the material.

3 Discussion

As a first application of the formalism presented above, we considered arrangements of Cu atoms in bulk fcc Cu. We computed the band energies of n -atom subclusters, $E_{i_1 \dots i_n}^n$, using multiple-scattering theory. (The band energy is the term in Eq. 2 proportional to E . In the bulk, this is sufficient to demonstrate the convergence properties of the MST density expansion of Eqs. 4 and 5.) In Fig. 1 we show the irreducible two-atom band energy, E_{ij}^2 , for n th nearest-neighbor pairs of atoms as a function of the distance between the pair. The first- and second-nearest-neighbor pairs clearly dominate. In Fig. 2 we show the irreducible band energies, $E_{i_1 \dots i_n}^{(n)}$, for a line of Cu atoms in the [110] direction and for an octahedron of Cu atoms. In both cases, the irreducible energies tend to zero in a slightly oscillatory manner. Both of these figures demonstrate that our irreducible decomposition of the energy has desirable properties for simulations based on Eq. 1.

4 Acknowledgment

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Figure Captions

Fig. 1 Irreducible two-atom energies for n th nearest-neighbor pairs of atoms in bulk Cu as a function of distance between the atoms.

Fig. 2 Irreducible energies for n -tuples of atoms in bulk Cu. Squares points are for atoms along a line in the $[110]$ direction; circles are for an octahedral arrangement of atoms.

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