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A Tight-Binding Method for the Evaluation of the Total Energy of Large Systems[1]

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A new tight-binding total energy method, suitable for the description of atomic systems containing hundreds of atoms, is described. The method is applied to the calculation of the vacancy-formation energy in the noble metals and several transition metals. The method agrees reasonably well with experiment, even though no information about the vacancies was used in constructing the tight-binding Hamiltonian.

KEY WORDS: copper; first-principles calculations; gold; metals; molybdenum; niobium; silver; tight binding; vacancy-formation energy.

1. INTRODUCTION

The development of high-speed computers and fast algorithms for solving differential equations has allowed first-principles electronic structure theory to make tremendous strides in the past decade. Given a crystal structure, it is now possible to calculate accurately total energies of atoms, molecules, clusters, and solids. The resulting energy surfaces can be used to predict mechanical properties such as the equilibrium density [1], elastic constants [2], vacancy-formation energies [3–7], and phonon frequencies [8]. Computations involving several crystal structures provide input for the construction of structural phase diagrams [9].

Given these successes, it is natural to attempt to use first-principles methods to understand the structure of real materials, including the properties of surfaces, defects, stacking faults, complex alloys, and amorphous

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solids. While these computations must necessarily consider the lattice to be static, they could also be used as input for molecular dynamics simulations to study liquids and phase transitions and to perform quantum path integral simulations. These calculations will require structural information for systems containing thousands of atoms. This is beyond the grasp of current first-principles methods, since the time to perform an electronic structure calculation is proportional to the cube of the number of atoms in the system, giving rise to the so-called "$O[N^3]$" problem. While various techniques [10, 11] have been proposed to avoid this problem, none is fully developed, nor have any been shown to work for metals and intermetallic alloys, the area of our principal interest.

What is needed, then, is an accurate approximate method for obtaining structural energies in many-atom systems. Several methods have been tried. One of the most successful is the embedded atom method (EAM) [12, 13], which uses first-principles total energies and experimental data to fit physically reasonable embedding and pair-potential functions. These functions can then be used to calculate structural properties in large systems. The EAM has been used successfully in many systems; however, it must be modified to handle systems with covalency, such as bcc metals.

Another approach, which we explore here, is to use the electronic structure information provided by the first-principles calculations, in conjunction with the total energies, to provide an approximation of the quantum mechanical nature of the electronic structure. We use the framework of the tight-binding formulation of quantum mechanics to develop a method by which first-principles calculations can be used to determine a set of tight-binding parameters which can be used to construct a Hamiltonian for extended systems. The method provides the total energy and electronic structure of the extended system.

The method is described briefly in Section 2. We then apply it to a large-scale problem, the calculation of the vacancy formation energy, in Section 3. We make some concluding remarks in Section 4.

2. THE TIGHT-BINDING TOTAL ENERGY METHOD

The tight-binding method used here has been discussed elsewhere [14, 15]. We will use this section to present a brief summary of the model. Standard tight-binding theory [16] evaluates the electronic structure using a basis of localized orbitals centered on each atom. These matrix elements can be used to form a Hamiltonian matrix H which is sparse for large systems, i.e., most matrix elements are zero. If the basis functions are nonorthogonal, there is a corresponding overlap matrix S which must also be constructed. The overlap matrix is also sparse for large systems. The electronic structure problem then reduces to the standard problem of solving the generalized eigenvalue problem

$$H\,|n\rangle = \varepsilon_n S\,|n\rangle \tag{1}$$

for eigenvalues ε_n and eigenstates $|n\rangle$. Note that the tight-binding method is much faster than the full-potential linearized augmented plane wave (LAPW) method [17, 18] or the muffin-tin augmented plane wave (APW) method [1]. These more accurate methods require on the order of 50–100 basis functions per atom, while a tight-binding calculation which includes s, p, and d orbitals requires only 9 basis functions per atom. Using the N^3 rule to approximate the computational difficulty, we see that tight-binding methods can be 1000 times faster than first-principles electronic structure methods. Sparse matrix techniques will give tight-binding methods an even larger edge.

Parametrized tight-binding methods [19] use the tight-binding formalism as a framework for approximating the electronic structure. The nonzero elements of H and S are considered to be parameters, and are fit to reproduce the electronic structure from first-principles calculations of simpler systems [20–23]. Consider the Kohn–Sham [24] formulation of density functional theory [25]. One writes the total energy of an electronic system in the form

$$E[n(\mathbf{r})] = \sum_{\text{occ}} \varepsilon_i + F[n(\mathbf{r})] \tag{2}$$

where $n(\mathbf{r})$ is the density of electrons, ε_i are the eigenvalues of the single-particle Schrödinger equation, and $F[n(\mathbf{r})]$ is a functional of the density which includes kinetic, Coulomb, and exchange-correlation effects which are not included in the eigenvalue sum. Note that the summation is only over the occupied states of the Hamiltonian. In tight-binding calculations, the parameters are chosen to fit the ε_i as determined from electronic structure calculations. The remaining term, $F[n(\mathbf{r})]$, is approximated by a sum of pairwise potential functions connecting the atoms in the solid.

While reasonably successful, this approach has some conceptual difficulties. Consider a shift of the eigenenergies by an amount V_0 (equivalent to a uniform shift of the potential energy), which forces F to change by an amount $N_e V_0$, where N_e is the number of electrons in the system. The pair potentials used to approximate F can be attractive or repulsive, depending on the algorithm used to choose V_0. Fortunately, the freedom to choose V_0 allows us to eliminate the pair potentials completely. We define a set of shifted eigenvalues,

$$\varepsilon_i' = \varepsilon_i + F[n(\mathbf{r})]/N_e \tag{3}$$

These are obviously independent of the choice of V_0. The total energy is thus

$$E[n(\mathbf{r})] = \sum_{\text{occ}} \varepsilon_i' \tag{4}$$

We now sketch the development of our tight-binding parametrization. First-principles total energy calculations are performed for simple monatomic structures. We use either the full-potential linearized augmented plane wave (LAPW) [17, 18] or the muffin-tin potential augmented plane wave (APW) [1] method. In the case of the metals discussed here we used only 3–5 structures in each of the fcc and bcc lattices. The electronic band structures and total energies were tabulated as a function of volume, and used to calculate the shifted band energies ε_i'.

The hopping terms in the Hamiltonian and overlap matrices are assumed to have the form

$$P_i(r) = (a_i + b_i r)\exp[-c_i^2 r]\, f(r) \tag{5}$$

where r is the distance between atoms and $f(r) = \{\exp[(r - r_0)/l] + 1\}^{-1}$ is a universal cutoff function which is chosen to allow all the functions to vanish smoothly at large r. Typically we take $r_0 = 16.5$ Bohr and $l = 0.5$ Bohr. We restrict ourselves to $l = s$, p, and d orbitals, whence there are ten hopping terms P_i per atom for each Hamiltonian and overlap matrix.

On-site terms are controlled by the "density" of neighboring atoms:

$$\rho_k = \sum_j \exp[-d_{\bar{j}\bar{k}}^2 r]\, f(r) \tag{6}$$

where $d_{\bar{j}\bar{k}}$ depends on the atom types (atom j has type $\bar{j}$). The on-site parameters, which set the energy scale, are fitted to a finite-strain approximation polynomial:

$$D_{i\bar{k}} = \varepsilon_{i\bar{k}} + g_{i\bar{k}}\rho_k^{2/3} + h_{i\bar{k}}\rho_k^{4/3} \tag{7}$$

The 70 parameters needed in this method are determined to give the best simultaneous fit to the electronic structure and total energies calculated from the input first-principle calculations. Generally the RMS error of the occupied bands is on the order of 5 mRy (1 Ry = 13.6 eV), and the RMS error of the energies is on the order of 0.5 mRy.

We have tested this method by constructing parameters for several transition and noble metals, then using the parametrization to determine the energy/volume relationships for several phases of each metal, the elastic constants, and the phonon spectra [14, 15]. As discussed above, these

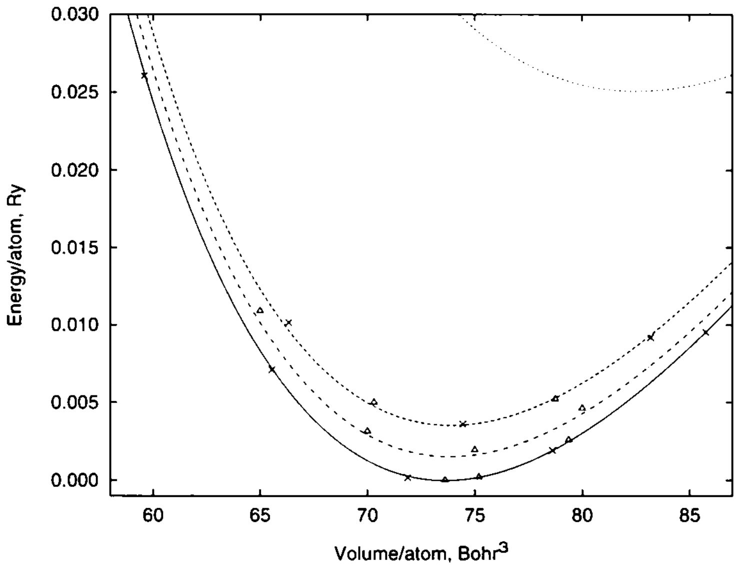

Fig. 1. Comparison of Tight-Binding and LAPW energy/volume predictions for several phases of Copper. The lines denote the tight-binding calculations: fcc (solid), bcc (dashed), hcp (dash-dot), and simple cubic (dotted). Marked points indicate first-principles full-potential LAPW calculations. The "×" represent the fcc and bcc volumes used in fitting the tight-binding parameters, while fcc, bcc, and hcp points not used in the fit are marked by "Δ." The energies for the LAPW simple cubic phase are at approximately 0.040 Ry and are not shown on this graph.

calculations are about 1000 times faster than the corresponding first-principles calculations [2, 8], but are of comparable accuracy. As an exaple, in Fig. 1 we compare full-potential LAPW calculations with the tight-binding results for the fcc, bcc, hcp, and simple cubic phases of copper. Note that our tight-binding parametrization correctly places the hcp and sc phases on the diagram *without fitting them.*

3. VACANCY-FORMATION ENERGY

Point defects in metals are of interest in materials physics. In particular, the interaction of point defects and dislocations determines the ductility of a metal. Unfortunately, because of the long-range interaction between point defects, it is difficult to describe them accurately using exact first-principles methods. For example, in a study of vacancy formation in aluminum [3], it was found that a 27-atom supercell did not adequately isolate the vacancy, while computations involving larger unit cells are difficult to fit on current computers. Calculation of vacancy-formation energies by the tight-binding method is rather easy, however. Furthermore, since many experimental vacancy-formation energies are known [26], we can use these calculations to test the accuracy of the tight-binding results for many-atom systems.

We use the supercell method to obtain the vacancy-formation energy. For example, to calculate the vacancy-formation energy in silver, we construct an N-atom supercell of the fcc lattice, removing one atom from the supercell to form the vacancy. Since the supercells themselves form a periodic lattice, there is an interaction between the vacancies which vanishes in the limit of large N. The energy required to form the vacancy in the N-atom supercell is given by

$$E_{\mathrm{vacancy}}(N) = E(N-1, 1) - \frac{N-1}{N} E(N, 0) \tag{8}$$

where $E(N-M, M)$ is the total energy of an N-site supercell with M vacancies. The supercell vacancy-formation energy $E_{\mathrm{vacancy}}(N)$ approaches the true vacancy-formation energy in the limit of large N.

We calculated the vacancy-formation energy for Cu, Ag, Au, Nb, and Mo, using supercells of up to 216 atoms with the tight-binding method described in Section 2. In most cases the vacancy-formation energy converged at 108 atoms. We first did the calculations without allowing the atoms near the vacancy to relax, and then allowing the vacancies' first and second nearest neighbors to relax to the minimum-energy structure. The resulting vacancy-formation energies are shown in Table I, along with the experimental results [26]. There is reasonable agreement with experiment, especially considering the large discrepancy between different types of experimental measurements. Also, we note that the tight-binding method

Table I. Vacancy-Formation Energy as Calculated by the Tight-Binding Method Described in the Text and Compared to Experiment

	Vacancy-formation energy (eV)		
	Tight-binding		
Element	Fixed	Relaxed	Experiment[26]
Cu	1.29	1.18	1.28–1.42
Ag	1.31	1.24	1.11–1.31
Au	1.24	1.12	0.89
Nb	2.84	2.82	2.07–2.65
Mo	2.26	2.15	3.0–3.6

correctly predicts the *qualitative* difference between the noble fcc metals, where the vacancy-formation energy is on the order of 1 eV, and the bcc transition metals, where vacancies require over 2 eV to form.

4. SUMMARY

We have presented a brief discussion of a new method for obtaining tight-binding parametrizations for metals, and shown how the method can be applied to large unit cells by calculating the vacancy-formation energies for several metals. In the future we will extend the tight-binding method to include binary interactions so that a wide variety of intermetallic alloys can be considered.

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