

TIGHT-BINDING POTENTIALS FOR FCC METALS

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ABSTRACT

A novel semiempirical tight-binding potential to simulate properties of fcc metals is proposed. The novelty lies in the fact that the attractive part of the potential is of the form of an n th power dependence on the effective coordination (or second moment of the local density of states) instead of the usual fixed choice for n ($1/2$ or $2/3$). The repulsive part of the interaction potential is, of course, the standard Born-Mayer type. In order to use this potential for specific metallic solids, the model parameter n and four other parameters are fitted on an equal footing to experimental data. It turns out that the parameter n is not a constant for all metals. This work furnishes an alternative prescription for determining tight-binding potentials.

1. INTRODUCTION

A fast and accurate method of calculating total energies or defect energies is desirable for the study of systems of interest to the material scientist. These are large or small systems including surfaces, extended defects, complex alloys and involving a total or partial loss of periodicity. Due to the enormous computational burden posed by these systems, ab initio methods [1-9] or fast self consistent calculational techniques [10,11], which are the ideal theoretical framework for handling these systems, may not be convenient computational methods given the current state of our technology. During the last two decades several semi empirical potentials [12-29] that include many-body interaction terms, beyond a pair potential term, have been developed. These semiempirical approaches have been found to provide fairly accurate results with considerably increased computational efficiency compared to first principles or ab-initio approaches. For instance, it is now widely recognized that semiempirical many-body potentials can reproduce with good accuracy the thermodynamic and structural properties of several metals. In the last years, these potentials have been extensively used to analyze a variety of problems in materials science, sometimes with the help of molecular-dynamics computer simulation techniques. It appears then that the only practical way, currently, to approach the simulation of point or extended defects (vacancies, grain boundaries, or dislocations), interfaces, and surface properties for metals and intermetallic alloys, is through the use of semi empirical potentials.

In general, semi empirical approaches tackle the many-body problem by determining a functional form, for the cohesive energy, based on some physical model. The functional form often contains some parameters, which are to be determined by fitting to experimental properties. Once these parameters have been determined, the functional form may then be used to calculate various other properties, such as defect energies, etc.

The main advantage of a many-body empirical potential treatment over the traditional and practically simpler pair-potential treatment is the ability to better reproduce some basic features of metallic systems. First of all, the so-called Cauchy discrepancy of the elastic constants, namely, the experimental evidence that for most cubic crystals $C_{12} \neq C_{44}$, cannot be accounted for by pair potentials. Another serious drawback of the use of pair potentials is represented by the incorrect estimates of the mono vacancy formation energies, whose predicted values result very nearly equal to the cohesive energies, whereas the experimental results indicate that they range around $\frac{1}{3}$ of the cohesive energy. Furthermore, stacking fault energies, surface structure, and relaxation properties cannot be properly accounted for by means of pair potentials. A many-body potential scheme usually overcomes these difficulties by including, even at a phenomenological level, the essential aspects of the metallic bond that are absent in the pair-potential scheme.

A relatively simple scheme for relating the atomic and electronic structure of metals, without resorting to the complex treatment of first principles calculations, is the tight-binding (TB) theory of cohesion [30-33]. The second moment approximation (SMA) of the TB theory expresses the cohesive energy of a metallic solid as a sum of two terms, one coming from the band energy E_B (the attractive term) and the other term, E_R , being a repulsive contribution. In this TB-SMA scheme [22-29,34-36] the interaction between two atoms depends on the interatomic distance and also on the local environment around each atom. Improvements over the SMA have been proposed, first by Carlsson [37] and later by related approaches [26-29,38] adding other attractive terms to the cohesive energy. These additional terms depend on higher moments of the density of states (DOS) in order to incorporate contributions to the energy from changes in the shapes of the DOS.

On the whole the TB-SMA scheme contains five model parameters, usually denoted as A , ξ , p , q , and n . These parameters can be determined by fitting to the experimental values of the cohesive energy, the mono vacancy formation energy, and the independent elastic constants, and also by taking the equilibrium conditions into account.

In several applications of the TB-SMA scheme, the model parameter n is often taken as 0.5. With such a choice, Cleri and Rosato [25] determined the values of the other four parameters for several metals, by fitting to the experimental cohesive energy E_C , the bulk modulus B_0 , the elastic constant C_{44} , and also by taking the equilibrium condition into account. For several metals, the predicted values of the monovacancy formation energy E_n^f as well as the other elastic constants (C_{11} and C_{12}) disagreed with the experimental values.

Guevara et al [26] on the other hand chose the value of n to be $\frac{2}{3}$ and their best tight-binding potential was obtained by fitting to the experimental cohesive energy E_C , the monovacancy formation energy E_n^f , the Bulk modulus B_0 , and also taking the equilibrium condition into account. Again for several metals the predicted values of the elastic constants turned out to disagree with the experimental values.

In this paper, I set out to treat the parameter n on an equal footing with the other four parameters, disregarding the theoretical justifications behind the choice of $n = 1/2$ or $n = 2/3$. That is, the five parameters in the TB-SMA scheme have been determined by fitting to the experimental value of E_C , E_n^f , B_0 , $C_{12} - C_{44}$, and also taking the equilibrium condition into account. It is shown in the text that the value of the parameter n does not come out to be a constant for the four typical FCC metals (Ni, Cu, Au, and Pd), whose potentials are explicitly exhibited. At the same time the new potentials lead to good agreement with experiment in the physical quantities whose values are predicted. This work therefore provides an alternative prescription for determining tight-binding potentials.

This paper is organised as follows: in section 2, the basic equations of the theory relevant to this work are presented in section 3, results are reported for four typical FCC metals; finally, concluding remarks are given in section 4.

2. THEORY

It has been pointed out by Cleri and Rosato [25] that the TB-SMA scheme is formally analogous to the embedded-atom method (EAM) scheme. The details of the EAM, which can be found in references [12] and [39-41], are skipped here. However, the 7 basic equations that frequently arise when working practically with the EAM are given below. Such a presentation will facilitate our contact with the TB-SMA scheme later. Starting with a general cohesive function $U(r)$ which is a sum of two terms one gets in a nearest-neighbour model for FCC metals the equations:

$$U_0 = 6\phi_1(r_0) + F(\rho_e) \quad (2.1)$$

$$0 = 6\phi_1'(r_0) + F'(\rho_e)[\rho'(r_0)] \quad (2.2)$$

$$\frac{9}{2}aB_0 = 6\phi_1''(r_0) + F''(\rho_e)[\rho'(r_0)]^2 + F'(\rho_e)[\rho''(r_0)] \quad (2.3)$$

$$\frac{a}{4}C_{11} = \left[\frac{\phi_1'(r_0)}{2r_0} + \frac{\phi_1''(r_0)}{2} \right] + \frac{aF'}{4\Omega_0}(\rho_e)W_{11} + \frac{a}{4\Omega_0}F''(\rho_e)V_{11}^2 \quad (2.4)$$

$$\frac{a}{4}C_{12} = \left[\frac{-5\phi_1'(r_0)}{4r_0} + \frac{\phi_1''(r_0)}{4} \right] + \frac{aF'}{4\Omega_0}(\rho_e)W_{12} + \frac{a}{4\Omega_0}F''(\rho_e)V_{11}^2 \quad (2.5)$$

$$\frac{a}{4}C_{44} = \left[\frac{-5\phi_1'(r_0)}{2r_0} + \frac{\phi_1''(r_0)}{4} \right] + \frac{a}{4\Omega_0}F'(\rho_e)W_{12} \quad (2.6)$$

$$E_n^f = 12F(11\rho_e/12) - 11F(\rho_e) - U_0 \quad (2.7)$$

In the equations above, U_0 is the equilibrium energy per atom, i.e., the negative of the experimental cohesive energy. B_0 and C_{ij} are, respectively, the bulk modulus, and the

elastic constants written in the Voigt notation. Ω_0 is the volume per atom in the solid, r_0 is the equilibrium nearest-neighbour distance, and a is the equilibrium lattice constant. ϕ_1 is a repulsive pair potential whose first and second derivatives with respect to the radial distance r are, respectively, ϕ_1' and ϕ_1'' (all quantities being evaluated at $r = r_0$); while F' and F'' are the first two derivatives of the embedding function F with respect to the density, again all quantities being evaluated at the equilibrium density ρ_e . E_n^F is the mono vacancy formation energy, while V_{11} , W_{11} and W_{12} are EAM parameters.

In all of our previous applications of the EAM [39-41], V_{11} , W_{11} and W_{12} have been considered as free parameters to be consistently determined so that the basic equations of the EAM are satisfied. Such an approach enables us to overcome the problem of the elastic constants not being correctly reproduced theoretically (see, for instance, [42-45]). We shall pursue a slightly different approach here, since it is often desirable to predict several physical quantities from a minimum set of parameters.

For an FCC lattice, $r_0 = a/\sqrt{2}$ and $\Omega_0 = a^3/4$, and expressions for V_{11} , W_{11} and W_{12} in terms of the derivatives of the density may be got from reference [12] or [46], after some algebra, in the form

$$V_{11} = r_0 \rho'(r_0)/3 \quad (2.8)$$

$$W_{11} = \frac{a^2}{12} [\rho''(r_0) + \rho'(r_0)/r_0] \quad (2.9)$$

$$W_{12} = \frac{a^2}{24} [\rho''(r_0) - 5\rho'(r_0)/r_0] \quad (2.10)$$

It is clear from Eqns. (2.1) to (2.10) above that the EAM has three basic functions, i.e., $\phi_1(r)$, $F(\rho)$, and $\rho(r)$ which generate the 8 EAM parameters: $\phi_1(r_0)$, $\phi_1'(r_0)$, $\phi_1''(r_0)$, $F(\rho_e)$, $F'(\rho_e)$, $F''(\rho_e)$, $\rho'(r_0)$, and $\rho''(r_0)$.

All other parameters like V_{11} , W_{11} and W_{12} are dependent on these eight. The experimental input data required for the solution of the 7 EAM equations are the cohesive energy E_c ($= -U_0$), the lattice constant a , the bulk modulus B_0 , the three independent elastic constants (C_{11} , C_{12} , and C_{44}), and the monovacancy formation energy E_n^F . The determination of the 8 EAM parameters, in the absence of explicit functional forms for the three basic EAM functions, is a nontrivial problem and the interested reader should consult the relevant literature [12-13, 39-41]. Suffice it to state here that once the 8 EAM parameters have been determined, then various other physical quantities of interest can be determined from our knowledge of the functions $\phi_1(r)$, $F(\rho)$, and $\rho(r)$.

In an obvious correspondence with the EAM scheme, the expression for the cohesive energy U_0 in the TB-SMA scheme is

$$U_0 = E_R + E_B \quad (2.11)$$

where the functions E_R and E_B can be written in a generalized form as

$$E_R \equiv 6 \phi_1(r) = A \sum_j \exp[-p(r_j/r_0 - 1)]$$

and

$$E_B \equiv F(\rho) = -\xi \left(\sum_j \exp[-2q(r_j/r_0 - 1)] \right)^n \quad (2.13)$$

It is clear that the density function $\rho(r)$ is

$$\rho(r) = \sum_j \exp[-2q(r_j/r_0 - 1)] \quad (2.14)$$

and hence (2.13) can be recast in the form

$$E_B \equiv F(\rho) = -\xi(\rho)^n \quad (2.15)$$

The sum over j in Eqns. (2.12) to (2.14) is actually a sum over neighbours r_{ij} being the distance between atom j and atom i (the reference atom). In this study the summation was carried out up to the 5th nearest neighbour.

The TB-SMA expressions for the functions $\phi_1(r)$, $F(\rho)$ and $\rho(r)$ as contained in the Eqns. (2.12) to (2.14) are governed by only 5 parameters [A , p , ξ , q and n], instead of the 8 parameters

$[\phi_1(r_0), \phi_1'(r_0), \phi_1''(r_0), F(\rho_e), F'(\rho_e), F''(\rho_e), \rho'(r_0)$ and $\rho''(r_0)]$ which are encountered in the EAM scheme. Hence, the 7 EAM equations can be immediately solved if we substitute the expressions (2.12) to (2.14) and their derivatives for the functions $\phi_1(r)$, $F(\rho)$, $\rho(r)$ and their derivatives, encountered there. That is, the TB-SMA scheme developed here has a total of 5 parameters that must be determined from the 7 equations (2.1) to (2.7).

In the initial development of the TB-SMA scheme, the 5 basic parameters were determined by fitting results from ab initio calculations for high symmetry structures, the only experimental input being the lattice constant. The fitting procedure is quite cumbersome since the ab initio results are not so easily available. Physical quantities like the elastic constants, the vacancy formation energy, etc., were subsequently predicted by the theory. Unfortunately this ambitious program [28-29] is yet to reach the much desired perfection stage, since several predicted quantities are still in conflict with experiment.

In several applications of the TB-SMA scheme the parameter n is specified a priori to be $\frac{1}{2}$ or $\frac{2}{3}$ [22, 25, 26]. In this situation the four remaining free parameters of the TB-SMA scheme can be determined from the EAM equations either using Eqs. (2.1), (2.2), (2.3) and (2.7) or Eqns. (2.1), (2.2), (2.3) and any one of (2.4) to (2.6). We pursue a different approach in this study. The parameter n and the four others are determined on an equal footing from Eqs. (2.1), (2.2), (2.3), (2.7) and the equation

$$\Omega_0(C_{12} - C_{44}) = F''(\rho_e) V_{11}^2 \quad (2.16)$$

which is got directly from (2.5) and (2.6).

3. RESULTS

The results presented here for FCC Cu, Ni, Au and Pd are preliminary. Much more comprehensive results covering several metals will be reported in the future. The general problem studied here is the problem of determining tight-binding potentials for FCC metals within a generalized TB-SMA scheme. The five parameters of the TB-SMA scheme, as determined in this study, are exhibited in Table 1, along with those obtained from other studies [25,26]. The first row for each metal shows the parameters obtained by Cleri and Rosato [25]. The second row gives the parameters obtained by Guevara et al [26], while the third row gives the parameters obtained in this study.

Table 2 displays the experimental data used for the parameter determination of the tight-binding potentials, and the three elastic constants predicted from the potentials. Clearly the agreement with experiment is quite good. This work therefore provides an alternative prescription for determining the tight-binding potentials. It has already been stated that the results presented here are preliminary. The results are, in fact, part of a much more comprehensive study, currently going on, to try to answer four important questions:

- (i) How well do the TB-SMA parameters, obtained via the prescription reported in this study, perform in reproducing the results of ab initio total energy calculations? It must be recalled that the parameters of the TB-SMA scheme are often determined by reference to ab initio total energy calculations [27-29].
- (ii) How well do the parameters of the new generalized TB-SMA scheme perform in correctly reproducing the various physical properties of pure FCC metals, alloys, and defects?
- (iii) How sensitive are the parameters (and calculated results) to the number of neighbours taken into account in the definition of the functions $F(\rho)$, $\phi_1(r)$, and $\rho(r)$ [see Eqns. (2.12) to (2.14)]?. In this study the summation over j in these equations was carried out up to the 5th nearest-neighbour.
- (iv) How well will this new generalized scheme perform for bcc metals? According to Cleri and Rosato [25], the application of their TB-SMA scheme (i.e., $n = \frac{1}{2}$ type potentials) to bcc transition metals was found to be unsuccessful.

TABLE 1: Parameters of the Tight-binding Potentials

Metal	Reference	n	A (eV)	ξ (eV)	P	q
Cu	[25]	1/2	0.0855	1.224	10.960	2.278
	[26]	2/3	0.270	1.222	7.345	2.562
	This study	0.5075	0.0884	1.2003	10.8107	2.3000
Ni	[25]	1/2	0.0376	1.070	16.999	1.189
	[26]	2/3	0.344	1.544	7.267	2.562
	This study	0.3881	0.0234	1.4682	21.0000	1.2319
Au	[25]	1/2	0.2061	1.790	10.229	4.036
	[26]	2/3	0.417	1.654	8.497	3.628
	This study	0.7242	0.5532	1.7038	8.3464	3.6739
Pd	[25]	1/2	0.1746	1.718	10.867	3.742
	[26]	2/3	0.318	1.443	9.076	3.317
	This study	0.7152	0.4301	1.5035	8.4250	3.3160

TABLE 2: Experimental data used for the parameter determination and calculated properties. The first five rows give the Experimental inputs: E_C , E_{IV}^F , a , B_0 , and $C_{12} - C_{44}$, taken from the compilation of Ref. [39]. The last three rows give the calculated or predicted quantities in this study, compared with experiment (the values in parenthesis).

Physical Quantity	Cu	Ni	Au	Pd
E_C (eV)	3.50	4.44	3.78	3.94
E_{IV}^F (eV)	1.30	1.60	0.96	1.40
a (Å)	3.61	3.51	4.07	3.89
B_0 (Mbar)	1.420	1.876	1.803	1.955
$C_{12} - C_{44}$ (Mbar)	0.431	0.191	1.243	1.049
C_{11} (Mbar)	1.913 (1.762)	2.741 (2.612)	2.084 (2.016)	2.390 (2.341)
C_{12} (Mbar)	1.172 (1.249)	1.466 (1.508)	1.663 (1.697)	1.720 (1.761)
C_{44} (Mbar)	0.740 (0.818)	1.275 (1.371)	0.420 (0.454)	0.671 (0.712)

4. CONCLUSION

A novel semi empirical tight-binding potential to simulate properties of fcc metals has been discussed in this study. The novelty lies in the fact that the attractive part of the potential is of the form of an n th power dependence on the effective coordination, and unlike other works in the literature, the value of n is not set a priori to be a constant for all metals. The five basic parameters of the generalized TB-SMA scheme were explicitly exhibited for four typical fcc metals – Cu, Ni, Au, and Pd. The predicted elastic constants for these metals were found to be in good agreement with experiment. This work therefore furnishes an alternative prescription for determining tight-binding potentials within the generalized TB-SMA scheme.

TABLE I. Physical quantities calculated for the four metals (Cu, Ni, Au, and Pd) using the generalized TB-SMA scheme. The values are given in parentheses. The values in parentheses are the values in parentheses.

Physical Quantity	Cu	Ni	Au	Pd
E_F (eV)	7.0	10.0	5.5	8.5
E_D (eV)	1.0	1.5	1.0	1.5
a (Å)	3.56	3.52	3.89	3.57
B (Mdyn)	0.001	0.001	0.001	0.001
$C_{11} - C_{12}$ (Mdyn)	0.001	0.001	0.001	0.001
C_{11} (Mdyn)	0.001	0.001	0.001	0.001
C_{12} (Mdyn)	0.001	0.001	0.001	0.001
C_{44} (Mdyn)	0.001	0.001	0.001	0.001

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