

Application of Second Moment Approximation Scheme to Tight-Binding Potentials for FCC Metals

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Abstract

A novel semi empirical 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 state) instead of the usual fixed choice for $n(\frac{1}{2}$ or $\frac{2}{3})$. 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.

Keywords: Local density of state, pair potential treatment, second moment approximation, embedded-atom method scheme, vacancy formation energy

INTRODUCTION

A fast-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 that involve total or partial loss of periodicity. Due to the enormous computational burden posed by these systems, ab initio methods or fast self-consistent calculation techniques 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 (Mookerjee, Chen, Kumar and Satter, 2010; Sutton, Finis and Pettifor, 2007) that include many-body interaction terms, beyond a pair potential term, have been developed. These semi empirical 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 twenty years, these potentials have been extensively used to analyse variety of problems in material science, sometimes with the help of molecular-dynamic computer simulation techniques (Baskes, 1992). 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

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surface properties for metals and inter-atomic alloys, is through the use of semi empirical potentials (Goringe, Bowler and Harmandez, 2001).

In general, semi empirical approaches tackle the many-body problem by terminating 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 treatment over the traditional and practically simpler pair potential treatment is the ability to better reproduce some basic features of metallic systems (Mookerjee, Chen, Kumar and Satter, 2010). 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 monovacancy formation energies, whose predicted values result very nearly equal to the cohesive energies, whereas the experimental results indicate that they range around $\frac{1}{2}$ 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 (Glanville, Paxton and Finis, 2008). 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 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 Carison (1991) and later by Mehel and Papaconstantopoulos (1996) 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 , ϵ_q , 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 (Smith *et al.*, 1991).

In several applications of the TB-SMA scheme, the model parameter n is often taken as 0.5. With such a choice, Rodriguez *et al.* (1993) 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_{IV}^F , as well as the other elastic constants (C_{11} and C_{12}) disagreed with the experimental values.

Goringe *et al.*, (2001) 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_{IV}^F , the Bulk modulus B_0 , 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, we set out to treat the parameter n on an equal footing with the other four parameters, disregarding the theoretical justifications behind the choice of $n = \frac{1}{2}$ or $n = \frac{2}{3}$. That is, the five parameters in the TB-SMA scheme have been determined by fitting to the experimental value of E_C , E_{IV}^F , B_0 , C_{12} - C_{44} , and also taking the equilibrium condition into account. It is shown in this research article 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 presented. 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.

THEORETICAL METHODS

It has been pointed out by Rodriguez et al (1993) that the TB-SMA scheme is formally analogous to the embedded-atom method (EAM) scheme. Eqs (2.1) to (2.7) are frequently used in EAM calculations and we will apply them to our TB-SMA scheme later.

$$U_0 = 6\Phi_1(r_0) + F(\rho_e) \quad (2.1)$$

Where U_0 is the equilibrium energy per atom, Φ_1 is a repulsive pair potential, r_0 is the equilibrium nearest neighbour distance, ρ_e is the equilibrium density and F is an embedding function with respect to the density. We have

$$0 = 6\Phi_1'(r_0) + F'(\rho_e) [\rho'(r_0)] \quad (2.2)$$

where Φ_1' is the first derivative of Φ_1 with respect to the radial distance r ($r = r_0$). We also have

$$\frac{9}{2}aB_0 = 6\Phi_1''(r_0) + F''(\rho_e)[\rho'(r_0)]^2 + F'(\rho_e)[\rho''(r_0)] \quad (2.3)$$

where Φ_1'' is the second derivative of Φ_1 with respect to r ($r=r_0$), a is the equilibrium lattice constant, B_0 is the bulk modulus, F' and F'' are respectively the first and second derivatives of F with respect to the density, ρ' and ρ'' are the first two derivatives of ρ with respect to r_0 (All quantities are evaluated at $r = r_0$). Next we have

$$\frac{a}{4}C_{11} = \left[\frac{\Phi_1'(r_0)}{2r_0} + \frac{\Phi_1''(r_0)}{2} \right] + \frac{aF'}{4\Omega_0}(\rho_e)W_{11} + \frac{a}{4\Omega_0}F''(\rho_e)V_{11}^2 \quad (2.4)$$

and

$$\frac{a}{4}C_{12} = \left[-\frac{5\Phi_1'(r_0)}{4r_0} + \frac{\Phi_1''(r_0)}{4} \right] + \frac{aF'}{4\Omega_0}(\rho_e)W_{12} + \frac{a}{4\Omega_0}F''(\rho_e)V_{11}^2 \quad (2.5)$$

where C_{11} and C_{12} are elastic constants, Ω_0 is the volume per atom in the solid, V_{11} , W_{11} and W_{12} are EAM parameters. We then have

$$\frac{a}{4}C_{44} = \left[\frac{-5\Phi_1'(r_0)}{2r_0} + \frac{\Phi_1''(r_0)}{4} \right] + \frac{aF'}{4\Omega_0}(\rho_e)W_{12} \quad (2.6)$$

and

$$E_{IV}^F = 12F(11\rho_e/12) - 11F(\rho_e) - U_0 \quad (2.7)$$

where C_{44} is an elastic constant and E_{IV}^F is the mono vacancy formation energy.

For an FCC lattice, $r_0 = a/\sqrt{2}$ and $\Omega_0 = a^3/4$, and expression for V_{11} , W_{11} and W_{12} in terms of the derivatives of the density (Daw and Baskes, 1984), may be written in the form

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

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

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

It is clear from Eqns. (2.1) to (2.10) that the EAM has three basic functions, i.e., $\Phi_1(r)$, $F(\rho)$, and $\rho(r)$ which generate the 8 EAM parameters: $\Phi_1(r\sigma)$, $\Phi_1'(r\sigma)$, $\Phi_1''(r\sigma)$, $F(\rho_e)$, $F'(\rho_e)$, $F''(\rho_e)$, $\rho'(r\sigma)$, and $\rho''(r\sigma)$.

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 $E_c (= -U\sigma)$, the lattice constant a , the bulk modulus $B\sigma$, the three independent elastic constants (C_{11} , C_{12} , and C_{44}), and the monovacancy formation energy E_{IV}^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 out of the scope of this work. 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 cohesive energy $U\sigma$ in the TB-SMA scheme is

$$U\sigma = E_R + E_B \quad (2.11)$$

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

$$E_R \equiv 6 \Phi_1(r) = A \sum_j \exp[-\rho(r_{ij}/r\sigma - 1)] \quad (2.12)$$

and

$$E_B \equiv F(\rho) = -\epsilon_v (\sum_j \exp[-2q(r_{ij}/r\sigma - 1)]) \quad (2.13)$$

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

$$\rho(r) = \sum \exp[-2q(r_{ij}/r\sigma - 1)] \quad (2.14)$$

and hence Eqn (2.13) can be rewritten in the form

$$E_B \equiv F(\rho) = -\epsilon_v(\rho) \quad (2.15)$$

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).

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 , ρ , ϵ_v , q and n], instead of the 8 parameters [$\Phi_1(r\sigma)$, $\Phi_1'(r\sigma)$, $\Phi_1''(r\sigma)$, $F(\rho_e)$, $F'(\rho_e)$, $F''(\rho_e)$, $\rho'(r\sigma)$, and $\rho''(r\sigma)$] which are encountered in the EAM scheme. Hence, the 7 EAM equations can be immediately solved if we substitute the expression (2.12) to (2.14) and their derivatives for the functions $\Phi_1(r)$, $F(\rho)$, $\rho(r)$ and their derivatives, encountered there (Mehel et al., 1996). 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 constant, the vacancy formation energy, etc. were subsequently predicted by the theory. Unfortunately, this ambitious program is yet to reach the much desired perfection stage, since several predicted quantities are still in conflict with experiment (Sutton et al, 2007).

In several applications of the TB-SMA scheme the parameter n is specified a priori to be $\frac{1}{2}$ or $\frac{2}{3}$ (Rodriguez et al 1993; Goringe et al., 2001). In this situation the four remaining free parameters of the TB-SMA scheme can be determined from the EAM equations either using Eqns. (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 Eqns. (2.1), (2.2), (2.3), (2.7) and the equation

$$\Omega\sigma (C_{12}-C_{44}) = F''(\rho_e) V^2_{11} \tag{2.16}$$

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

RESULTS AND DISCUSSION

The results presented here for FCC Cu, Ni, Au and Pd are preliminary findings . 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 shown in Table 1, along with those obtained from other studies (Rodriguez et al. 1993; Goringe et al. 2001).

TABLE 1: Parameters of the Tight-binding potentials

Metal	Reference	n	A(eV)	ξ (eV)	P	g
Cu	Rodrig 1993	1/2	0.0855	1.224	10.960	2.278
	Goringe2001	2/3	0.270	1.222	7.345	2.562
	This study	0.5075	0.0884	1.2003	10.8107	2.3000
Ni	Rodrig 1993	1/2	0.0376	1.070	16.999	1.189
	Goringe2001	2/3	0.344	1.544	7.267	2.562
	This study	0.3881	0.0234	1.4682	21.0000	1.2319
Au	Rodrig1993	1/2	0.2061	1.790	10.229	4.036
	Goringe2001	2/3	0.417	1.654	8.497	3.628
	This study	0.7242	0.5532	1.7038	8.3464	3.6739
Pd	Rodrig 1993	1/2	0.1746	1.718	10.867	3.742
	Goringe2001	2/3	0.318	1.443	9.076	3.317
	This study	0.7152	0.4301	1.5035	8.4250	3.3160

The first row for each metal shows the parameters obtained by Rodriguez et al.(1993). The second row gives the parameters obtained by Goringe et al, 2001), 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 potential. Clearly the agreement with experiments is quite good. This work therefore provides an alternative prescription for determining the tight-binding potentials.

TABLE 2: Experimental data used for the parameter determination and calculated properties.

Physical properties	Cu	Ni	Au	Pd
Ec(eV)	3.50	4.44	3.78	3.94
E_{IV}^f (eV)	1.30	1.60	0.96	1.40
a(A)	3.61	3.51	4.07	3.89
Bo (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)

The first five rows give the experimental inputs: E_C , E_{IV}^F , a , B_0 , C_{12} - C_{44} , taken from Foiles (1986). The last three rows give the calculated or predicted quantities in this study, compared with experiment (the values in parenthesis).

CONCLUSION AND RECOMMENDATION

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 shown for four typical FCC metals – Cu, Ni, Au and Pd. The predicted elastic constant 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.

The results are preliminary findings and it is recommended that more work be carried out on these or other FCC as well as BCC or HCP metals. The work should especially be directed towards answering the following 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 (Cohen et al., 1994; Mehel et al., 1996)
- (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 Rodriguez et al. (1993), the application of their TB-SMA scheme (i.e. $n = 1/2$) to BCC transition metals was found to be unsuccessful.

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