# Defect energies by semi-empirical tight binding methods without explicit pairwise term

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A novel description of unrelaxed defect energies without explicit pairwise terms in semi-empirical tight binding method was obtained for the first nearest neighbour interaction model. The total energy per atom in perfect lattice estimated from the experimental defect energies using this description is a measure of the accuracy of the potentials on the defect energies. Pair potentials, simplest embedding atom method and semi-empirical tight binding recursion method are applied to the vacancy formation and three principal surface energies of aluminium.

## 1. INRODUCTION

The reliable atomistic level simulation for investigating real materials should be achieved by the fast calculations of accurate interatomic potentials. O(N) methods are target for the practical usage on simulations, and many methods are proposed[1-4]. Their formulation is usually the sum of the empirically determined pairwise repulsive term and electronic bonding term. The accuracy and the range of validity of these schemes are usually determined by the structure energy difference. From the practical usage of the potentials the estimated defect energies are very important measure for their reliabilities. We have simple measures of the applied limits on defect energies for the pair potentials and embedding atom methods[5], whereas we don't have any well-defined one for newly developing O(N) potentials.

In this letter we will see that the unrelaxed defect energies are estimated with the calculated bonding energy but without the explicit pairwise term. Using experimental defect energies, the accuracy of the interatomic potential will be determined only by the bonding energies. This new measure applied to the classical pair potential, simplest form of the embedding atom method (EAM) and the semi-empirical tight binding (TB) recursion method, which is one of the attracting O(N) methods, on the vacancy formation and three principal surface energies of aluminium. We will discuss the factors for the better convergency shown in the semi-empirical tight binding recur-

sion method.

## 2. FORMULATIONS

We assume the first nearest neighbour interaction with unrelaxed defect structures, becasue of the small difference between relaxed and unrelaxed models and the dominant contributions of the first nearest interactions even in the further nearest neighbour models. The total energy for the semi-empirical TB methods is written in the sum of the repulsive term and bonding term, namely,

$$E_{total} = E_{repul} + E_{bond}. \tag{1}$$

The repulsive term includes every contribution which is not included in bonding term, such as exchange-correlation, non-orthogonality, or electrostatic interactions[6]. The repulsive term usually take to be pairwise as follows

$$E_{repul} = \sum_{allbond} \phi(R_{ij}). \tag{2}$$

Then the total energy per atom is written as

$$E_0 = z_0\phi_0 + E_{bond}^{atom}, \tag{3}$$

where $z_0$ is the coordination number of perfect lattice, $\phi_0$ and $E_{bond}^{atom}$ are equilibrium repulsive energy per bond and equilibrium bonding energy per atom respectively. Although the total energy of some potentials are fitted to the cohesive energy, we leave the total energy as it is for the following discussion.

The defect energy is defined by the energy difference between the initial perfect lattice and the

final defect lattice, namely,

$$E_{defect} = E_{total}^{defect} - E_{total}^{perfect}. \qquad (4)$$

Substituting eqns.(1) and (3) into eqn.(4) then we have

$$E_{defect} = -z_1\phi_0 + dE_{bond}^{defect} \qquad (5)$$

where $z_1$ is the number of broken bonds and $dE_{bond}^{defect}$ is the contribution from bonding term. The repulsive energies per bond should be the same as those of perfect lattice, because we take the assumptions of unrelaxed condition and pairwise interaction for $\phi(R)$. From eqns.(3) and (5), we will find a novel expression of the defect energy, namely

$$E_{defect} = -\frac{z_1}{z_0}\left(E_0 - E_{bond}^{atom}\right) + dE_{bond}^{defect}. \qquad (6)$$

Using this equation, reversely, we can estimate the total energy per atom from experimental defect energies and calculated bonding energies, but no explicit repulsive energies. We will explore specific cases for interatomic potentials, such as pair potentials, embedding atom method, and semi-empirical TB recursion method.

## 2.1. Pair potentials

The conventional pair potentials are thought as if $E_{bond}^{atom}$ and $dE_{bond}^{defect}$ vanish. Thus we have

$$E^{defect} = -\frac{z_1}{z_0}E_0 \qquad (7)$$

from eqn.(6).

For the vacancy formation energy, the $z_0$ nearest neighbours to the vacancy site have their coordination of $z_0 - 1$, then the total broken bond become $z_1 = z_0$. Thus the wrong estimation of the vacancy formation energies are extracted as

$$E^{defect} = -E_0. \qquad (8)$$

## 2.2. EAM

The simplest form of the EAM, which is lead from the second moment approximation[7,8], describe the bonding energy at equilibrium as follows

$$E_{bond}^{atom} = -\sqrt{z}|h_0|, \qquad (9)$$

where $|h_0|$ is the average hopping integral at equilibrium. For the calculation of eqn.(6), only the 0th order value of $|h|$ is necessary. Simplest estimation has been achieved by taking some specific shape of the repulsive and hopping integral functions, such as exponential, $\phi(R) \propto exp(-pR)$ and $h(R) \propto exp(-qR)$ respectively. Substituting these functions to eqn.(3) and taking the equilibrium condition at $R = R_0$, the bonding energy per atom and bonding energy of defect structures are described as follows,

$$E_{bond}^{atom} = \frac{-p/qE_0}{1 - p/q} \qquad (10)$$

and

$$dE_{bond}^{defect} = -\sum_i \frac{\sqrt{z_i} - \sqrt{z_0}}{\sqrt{z_0}}\frac{p/qE_0}{1 - p/q} \qquad (11)$$

where the summation is taken over the all site with bond numbers varying from the perfect lattice.

Vacancy formation energy is estimated by substituting eqns.(10) and (11) into eqn.(6) and the same way as in the pair potentials

$$E_{defect} = -z_0\frac{E_0}{(1 - p/q)z_0} \qquad (12)$$

$$-z_0\frac{\sqrt{z_0 - 1} - \sqrt{z_0}}{\sqrt{z_0}}\frac{p/qE_0}{(1 - p/q)}$$

$$\simeq -\frac{(2 - p/q)E_{bond}^{atom}}{(1 - p/q)2}, \qquad (13)$$

where the second equality follows by expanding to first order of $1/z_0$ as $\sqrt{z_0 - 1} - \sqrt{z_0} \simeq -1/2\sqrt{z_0}$. The same expression has been already obtained by Allan and Lannoo[9]. Using typical values of $p/q$, three or five[8], and the cohesive energy for $|E_0|$, we have a well known right relation between cohesive energy and vacancy formation energy, namely $E_v = 1/4 \sim 3/8E_c[10]$.

## 2.3. TB

The algorithm used for the semi-empirical TB recursion method is developed for the bond order potential[11], whose bond energy is equivalent to that of conventional site-diagonal tight binding recursion calculations. The bonding energy includes covalent bond energy and promotion energy[6]. The former is calculated by the recursion

Table 1: Total energy per atom estimated from the defect energies for pair potentials, EAM and TB. The number in parenthesis for TB indicates the moment order. The units are in $eV$

| potential | pair | EAM | TB(2) | TB(4) | TB(16) |
|---|---|---|---|---|---|
| vacancy | -0.69 | -1.43 | -5.24 | -4.10 | -4.37 |
| (100) | -1.73 | -3.85 | -5.74 | -4.62 | -4.74 |
| (110) | -1.66 | -3.70 | -5.52 | -4.68 | -4.80 |
| (111) | -2.00 | -4.31 | -6.01 | -5.08 | -5.17 |
| max deviation | 1.31 | 2.88 | 0.77 | 0.98 | 0.80 |

algorithm for a specific moment level and the latter by the sum of the products between the self-energy level and the electron number difference in each orbital between the isolated free atoms and the atoms in solid. For the moment calculation we need a tight binding parameter set for hopping integrals and self energies, which are extracted from the first principle calculations. For aluminium, we use the sp bonded model with the parameter set obtained from APW calculation by Papaconstantopoulos[12]. The calculation in detail was given in the previous paper[13].

Note that the bonding term is obtained only by the absolute values of the tight binding parameters and no other approximations are necessary such as the function shape of distant dependence. Also note that the semi-empirical tight binding recursion calculation with the second moment level is equivalent to the simplest EAM except the inclusion of the orbital dependent hopping integrals and the promotion energy. The electronic structures of atoms near defects are heavily distorted and then the energies are calculated under the assumption of the local charge neutrality, which was achieved by shifting the self energy levels with keeping the energy difference constant.

## 3. RESULTS

The total energies per atom estimated from defect energies for pair potentials, EAM and TB are shown in table I. The experimental values are $0.7eV$ for the mono-vacancy formation energy and $1140mJ/m^2$ for the surface energies. The surface energies are calculated by the supercell models with minimum unit areas. Thus the bro-

ken bonds are $8 = (4) + (4)$ and $6 = (3) + (3)$ for the first layer of (100) and (111) principal surfaces respectively, and $6 = (5)$ for the first layer plus (1) for the second layer of (110). The results of EAM are obtained from eqn.(??) with $p/q$ of two, which leads good estimation of the structure stabilities of wide range of sp bonded elements[14]. The results for TB are given for the 2nd, 4th and 16th moment orders as indicated by the numbers in parentheses.

All the total energies per atom estimated from experimental defect energies deviate from the experimental cohesive energy, $3.39eV$ for aluminium. Inversely using a specific value of the total energy per atom we can see how accurately the potentials estimate the defect energies. The deviation of EAM is the largest in all the potentials examined in this paper. Using the total energy per atom reproducing the appropriate vacancy formation energy, the surface energies are estimated to be anomalously small[15]. Using the right relation between $E_0$ and the vacancy formation energy in eqn.(13), the value of $p/q$ should be larger than two and the surface energies become much smaller. Adjustment of the function shapes and thus more appropriate relation between $E_0$ and the defect energies does not improve this relation drastically.

The deviations of the results of TB recursion methods are much smaller than those of other potentials. We will see how TB recursion methods achieved this improvement. At first, we notice that the deviations of estimated total energies per atom don't decrease as increasing the moment levels. Of course, the contribution from the higher recursion levels is important for reproducing other physical properties, such as elastic con-

stants and the structure energy difference. Due to the change in the coordination number near the defect structures, the useful moment theorem tells that the energy change is given to the first order by the second moment change (see eqn.(6.64) of [16]). The results in table I clearly indicates that the values of the defect energies should be largely controlled by the lowest recursion level. Thus we can discuss the difference between the EAM and the simplest TB(2). Except the automatic achievement of the local charge neutorality in EAM, which changes few percent of the bonding energy, there are two main improvements in TB comparing to EAM; more accurate description of the electron orbitals and additional promotion energy. The promotion energy reduces roughly 20% from the bonding energy, which is very large contribution. Even at the atoms near defects, however, this value alter only few percent from the perfect atoms. Therefore, the contribution of the promotion energy for the defect energy is not so dominant. The remaining effect is only the appropriate description of the electron orbitals. EAM use only one average hopping integrals, whereas the simplest TB(2) use the orbital dependency. Althought the effects of the orbital characters should be explored more carefully, the accuracy of the potentials, in other words the tight binding parameters, are determined only by the bonding energy calculation with the lowest recursion level and eqn.(6) under the assumption of the pariwise repulsive interactions.

## 4. CONCLUSIONS

The useful estimation of total energy per atom from the defect energies without explicit pairwise repulsive contribution was given under the unrelaxed and first nearest neighbour interaction model. The semi-empirical TB recursion methods improved the absolute value of the defect energies, but not sufficient. The increasing of the moment order did not reduce the error as expected from the moment theorem. More detail discussion revealed that the factor which improved the convergence is not due to the promotion energy.

The easiest way to reproduce the defect energies empirically is the including of the coordination dependence in the repulsive terms, because the non-orthogonality interactions are main con-

tributions in them[6]. If we use the coordination dependence in the repulsive term without any general formulation of the overlap integral, however, we will loose the physical background and transparancy of the potentials. The other way is the using of more appropriate tight binding parameter set for the orthogonal basis extracted from the first principle calculations, and/or the including of the d orbital interactions.

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