

Inverse Lattice Problem and Finnis-Sinclair Model*

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The lattice inversion method is used to construct the pair potential and the hopping integral in Finnis-Sinclair model. In the approach, the lattice sum of square hopping integral is assumed to be an exponential function versus the nearest-neighbour distance, with two parameters determined from the Cauchy discrepancy and the difference of the unrelaxed vacancy-formation energy with the sublimation energy. The individual hopping integral is inverted from the exponential function and the pair potential is inverted from the remaining part of total cohesive energy.

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The idea of evaluating pair potential from cohesive energy as a function of lattice separation was recently developed by Chen *et al.*¹⁻⁶ The cohesive energy is written as a sum over pair potential and inversion was applied to such a cohesion formalism. However, it is well known that the cohesive energy can not be expressed by a sum of pair potentials. In general, the pair potential model yields two major disagreements with experimental bulk properties. The first one is the Cauchy relation $C_{12} = C_{44}$ which is not true. The second one is the unrelaxed vacancy-formation energy. The pair potential model predicts it to be equal to sublimation energy, whereas experiments show that vacancy-formation energy is about one third of sublimation energy.

The Finnis-Sinclair model (FSM) solves the above problem by using the following cohesion equation⁷

$$E_{\text{coh}} = \frac{1}{2} \sum_{i \neq 0} \Phi(R_i) - \sqrt{n} \quad (1)$$

with

$$n = \sum_{i \neq 0} \rho(R_i), \quad \rho(r) = h^2(r),$$

where $h(r)$ is the effective hopping integral which includes the s - d hybridization. $\Phi(r)$ is the pair potential which contributes to the remained part of the cohesive energy.

In this letter, we present a method for constructing the pair potential and the hopping integral from the Cauchy discrepancy $C_{12} - C_{44}$, the unrelaxed vacancy-formation energy E_v and the universal equation of cohesion proposed by Rose, Smith, Guinea and Ferrante (RSGF) (constructed by equilibrium atomic-volume Ω_e , bulk modulus B and sublimation energy E_s).⁸ In the present approach, the lattice sum of square hopping integral is assumed to be an exponential function versus lattice parameter, with two parameters determined by the Cauchy discrepancy and the difference between unrelaxed vacancy-formation energy and the sublimation energy $E_s - E_v$. The individual hopping integral is then inverted from this lattice-summed energy as a

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function of lattice parameter. The calculation of the pair potential is similar. The advantages of the present approach are twofold: firstly, the suppositions about the functional forms of the pair potential and the hopping integral are replaced by the assumptions on their summed functions, and the summed ones are easier to be related to experimental properties or first-principles results than the individual ones themselves; secondly, the pair potential and the hopping integral are arbitrary-ranged, rather than up to the second-nearest neighbour distance in FSM.

In FSM (an approximation of the embedded-atom method) formalism, the elastic constants B (bulk modulus), G (tetragonal shear modulus) and C_{44} (rhombohedral shear modulus) of cubic crystal can be formulated as follows^{9,10}

$$B = \frac{1}{18\Omega_e} \left[\sum_{i \neq 0} R_i^2 [\Phi''_{\text{eff}}(R_i) - \frac{1}{R_i} \Phi'_{\text{eff}}(R_i)] + \frac{1}{2\sqrt{n_e^3}} \left[\sum_{i \neq 0} \rho'(R_i) R_i \right]^2 \right], \quad (2)$$

$$G = \frac{1}{4\Omega_e} \sum_{i \neq 0} \frac{X_i^2(X_i^2 - Y_i^2)}{R_i^2} \left[\Phi''_{\text{eff}}(R_i) - \frac{1}{R_i} \Phi'_{\text{eff}}(R_i) \right], \quad (3)$$

$$C_{44} = \frac{1}{2\Omega_e} \sum_{i \neq 0} \frac{X_i^2 Y_i^2}{R_i^2} \left[\Phi''_{\text{eff}}(R_i) - \frac{1}{R_i} \Phi'_{\text{eff}}(R_i) \right], \quad (4)$$

where R_i denotes the length of the position vector of site i , X_i, Y_i are the x and y components of the position vector R_i , Ω_e is the equilibrium atomic volume, n_e is the equilibrium lattice sums of the square hopping integral, $\Phi_{\text{eff}}(r)$ is the effective pair potential which is defined as

$$\Phi_{\text{eff}}(r) = \Phi(r) - \frac{1}{\sqrt{n_e}} \rho(r). \quad (5)$$

Thereby the Cauchy discrepancy can be written by

$$C_{12} - C_{44} = \frac{1}{36\Omega_e} \left[\sum_{i \neq 0} \rho'(R_i) R_i \right]^2 \left[\sum_{i \neq 0} \rho(R_i) \right]^{-\frac{3}{2}}. \quad (6)$$

In conjunction with the many-body potential of FSM, the unrelaxed vacancy-formation energy in the absence of lattice relaxation includes both the pair-breaking energy and the tight-binding energy:⁹

$$E_v = -\frac{1}{2} \sum_{i \neq 0} \Phi(R_i) - \sum_{i \neq 0} \left[\sqrt{n_e - \rho(R_i)} - \sqrt{n_e} \right]. \quad (7)$$

As a good approximation for fcc structure whose coordination number (=12) is much greater than 1, Eq.(7) can be approximated to first-order by

$$E_v = -\frac{1}{2} \sum_{i \neq 0} \left[\Phi(R_i) - \frac{1}{\sqrt{n_e}} \rho(R_i) \right] = -\frac{1}{2} \sum_{i \neq 0} \Phi_{\text{eff}}(R_i). \quad (8)$$

The difference of the sublimation energy with the unrelaxed vacancy-formation energy can be easily seen from Eqs.(1) and (8):

$$E_s - E_v = \frac{1}{2} \sqrt{\sum_{i \neq 0} \rho(R_i)}. \quad (9)$$

As a reasonable choice, the lattice sum of $\rho(r)$ is assumed to be an exponential function of the nearest neighbour distance:

$$\sum_{i \neq 0} \rho(R_i) = n_c \exp \left[-\alpha \left(\frac{R_1}{R_{1c}} - 1 \right) \right]. \quad (10)$$

Another lattice sum in Eq. (6) is found to be

$$\sum_{i \neq 0} R_i \rho'(R_i) = -n_c \alpha \frac{R_1}{R_{1c}} \exp \left[-\alpha \left(\frac{R_1}{R_{1c}} \right) \right]. \quad (11)$$

Noting that all the inputs are measured with equilibrium lattice, we obtain the two parameters from Eqs. (6) and (9):

$$\alpha = \sqrt{\frac{18\Omega_c(C_{12} - C_{44})}{E_s - E_v}} \quad \text{and} \quad n_c = 4(E_s - E_v)^2.$$

It has been known that as a semi-empirical formula the cohesive energy as a function of lattice constant can be represented by the RSGF equation:

$$E(R_1) = -E_s \left[1 + \sqrt{\frac{9B\Omega_c}{E_s}} \left(\frac{R_1}{R_{1c}} - 1 \right) \right] \exp \left[-\sqrt{\frac{9B\Omega_c}{E_s}} \left(\frac{R_1}{R_{1c}} - 1 \right) \right]. \quad (12)$$

The tight-binding energy in second-moment-approximation as a function of lattice parameter reads as

$$E_{\text{TB}}(R_1) = -2(E_s - E_v) \exp \left[-\frac{1}{2} \alpha \left(\frac{R_1}{R_{1c}} - 1 \right) \right]. \quad (13)$$

Therefore, the lattice sum of pair potential is analytically

$$\frac{1}{2} \sum_{i \neq 0} \Phi(R_i) = E(R_1) - E_{\text{TB}}(R_1). \quad (14)$$

Thus we have obtained two lattice sums of the square hopping integral and the pair potential. The individual functions can be obtained by using the lattice inversion method for fcc-type lattice^{2,4}:

$$F(R_1) = \sum_{n=1}^{\infty} w(n) f(\sqrt{n}R_1) \iff f(R_1) = \sum_{n=1}^{\infty} m(n) F(\sqrt{n}R_1), \quad (15)$$

where $w(n)$ is the number of atoms on the n th shell, $m(n)$ is the Möbius function on fcc lattice.

The experimental data of the lattice constants a_0 , the sublimation energy E_s , the unrelaxed vacancy-formation energy E_v and the elastic constants C_{12} , C_{44} for Cu, Ag and Au as the inputs of the present approach are taken from Ref. 11. The inverted results for hopping integrals and pair potentials for Cu, Ag and Au are plotted in Fig. 1 by comparison with those of Cleri *et al.*¹² It is shown in Fig. 1 that the present hopping integrals fall in with those of Cleri *et al.*, while the pair potentials are in some region negative and in some region positive and different with the purely repulsive pair potentials of Cleri *et al.* The pair potential of this shape may be due to the s -electrons contribution, which is featured with a substantial attractive well and an

oscillatory tail. This outline of the pair potential represents the behaviour of the *s*-electrons in the environment of the *d*-electrons, which is not considered in the model of Cleri *et al.*

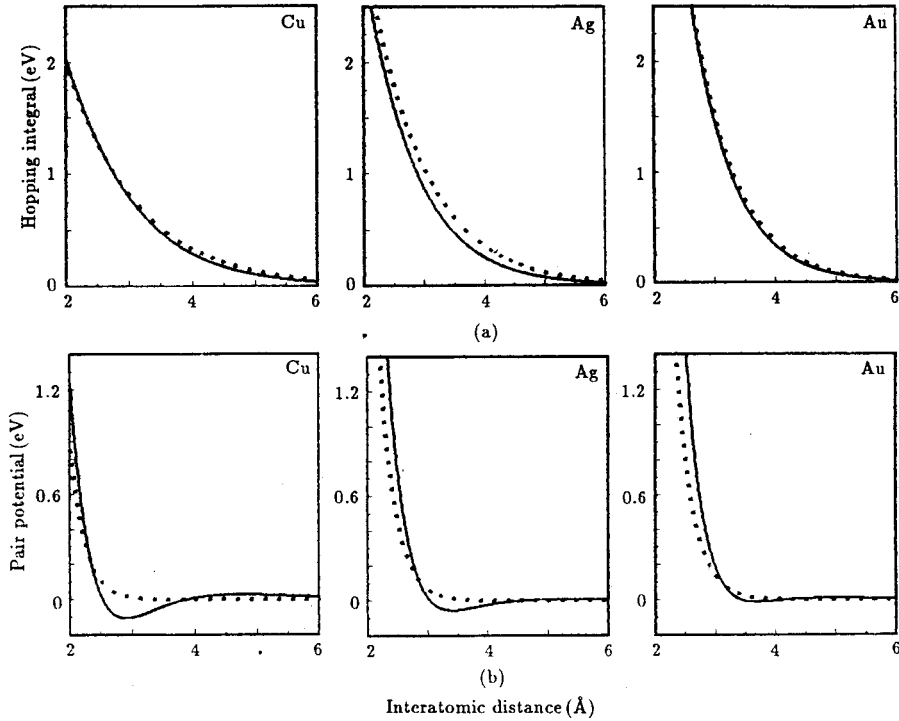


Fig. 1. Inverted effective hopping integrals and pair potentials for Cu, Ag and Au (the solid lines). The dashed lines are plotted according to Cleri *et al.*¹²

In summary, we have presented a method for constructing the hopping integral and the pair potential for the FSM. While it is at present semi-empirical, the approach is expected to incorporate useful information from first-principles calculation.

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