

Overview of interatomic potentials

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Abstract

In this report an overview on interatomic potentials is given. This overview is by no means complete and it has merely the intention to give the reader an idea of where interatomic potentials come from, as well as to provide the basic ideas behind some commonly used methods for deriving interatomic potentials for molecular dynamics applications.

We start by giving a short introduction about the concept of interatomic potential in the framework of quantum mechanics, followed by a short description of commonly used methods for deriving semi-empirical interatomic potentials. After some short theoretical notions on each method, some practical parameterizations of commonly used potentials are given, including very recent ones. An effort has been made to classify existing approaches within a rational and consequent scheme, which is believed to be of use for a thorough comprehension of the topic. Although these approaches can be used in a variety of different materials, we will only discuss the practical cases of metals. Following this, some widespread *ad hoc* modification of the general methods are discussed. The report is concluded by a generalization of the methods to multi-component materials, in particular metallic alloys.

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1 Introduction

Matter can be described as a system of interacting atoms, consisting of interaction electrons and nuclei. This ensemble of particles must be described quantum mechanically; it is in fact the Pauli principle in the electron-electron interaction that keeps matter from falling apart (see jellium calculations [1]).

Let us assume that a solid or molecule consists of N_{at} atoms with a total of N_{el} electrons. The evolution of this system in time can be described by the total many-body state $|\Psi_{tot}(t)\rangle$, or projected to coordination space the total wave function $\Psi_{tot}(\vec{R}_1, \dots, \vec{R}_{N_{at}}; \vec{r}_1, \dots, \vec{r}_{N_{el}}; t)$, with \vec{R}_α , $\alpha = 1, \dots, N_{at}$ the position vectors of the nuclei and \vec{r}_i , $i = 1, \dots, N_{el}$ the position vectors of the electrons and t the time variable. For simplicity the quantum numbers of the electrons are left away. This total time dependent state is described by the time dependent Schrödinger equation :

$$-i\hbar \frac{\partial}{\partial t} |\Psi_{tot}(t)\rangle = \hat{H}_{tot} |\Psi_{tot}(t)\rangle. \quad (1)$$

The formal solution of this equation is given by :

$$|\Psi_{tot}(t)\rangle = e^{-\frac{i}{\hbar} \hat{H}_{tot} (t-t_0)} |\Psi_{tot}(t_0)\rangle. \quad (2)$$

This solution is only meaningful if all the eigenvalues and eigenstates of \hat{H}_{tot} are known. So the time evolution of the system is completely determined by the solutions of the stationary Schrödinger eigenvalue equation :

$$\hat{H}_{tot} |\Psi_{tot,n}\rangle = E_{tot,n} |\Psi_{tot,n}\rangle, \quad \forall n. \quad (3)$$

The index n represents the possible eigenstates, i.e. the ground state and all possible excitation states. For simplicity the index n is left away in the following.

The total Hamiltonian is given by :

$$\hat{H}_{tot} = \hat{T}_N + \hat{T}_e + \hat{V}_{N-N} + \hat{V}_{e-e} + \hat{V}_{N-e}. \quad (4)$$

Herein the term \hat{T}_N represents the kinetic energy operator for the nuclei, \hat{T}_e the kinetic energy operator for the electrons, \hat{V}_{N-N} the potential energy operator for the Coulombic nucleus-nucleus interaction, \hat{V}_{e-e} the potential energy operator for the Coulombic electron-electron interaction and \hat{V}_{N-e} the potential energy operator for the Coulombic electron-nucleus interaction. Projected to coordination space these terms are given by :

$$T_N(\vec{R}_1, \dots, \vec{R}_{N_{at}}) = - \sum_{\alpha=1}^{N_{at}} \frac{\hbar^2}{2M_\alpha} \nabla_{\vec{R}_\alpha}^2 \quad (5)$$

$$T_e(\vec{r}_1, \dots, \vec{r}_{N_{el}}) = - \sum_{i=1}^{N_{el}} \frac{\hbar^2}{2m} \nabla_{\vec{r}_i}^2 \quad (6)$$

$$V_{N-N}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) = \frac{1}{2} \sum_{\alpha=1}^{N_{at}} \sum_{\beta=1}^{N_{at}} \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 |\vec{R}_\alpha - \vec{R}_\beta|}, \quad \alpha \neq \beta \quad (7)$$

$$V_{e-e}(\vec{r}_1, \dots, \vec{r}_{N_{el}}) = \frac{1}{2} \sum_{i=1}^{N_{el}} \sum_{j=1}^{N_{el}} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}, \quad i \neq j \quad (8)$$

$$V_{N-e}(\vec{R}_1, \dots, \vec{R}_{N_{at}}; \vec{r}_1, \dots, \vec{r}_{N_{el}}) = - \sum_{i=1}^{N_{el}} \sum_{\alpha=1}^{N_{at}} \frac{Z_\alpha e^2}{4\pi\epsilon_0 |\vec{R}_\alpha - \vec{r}_i|}. \quad (9)$$

The nuclear and electron masses are M_α and m respectively and Z_α is the atomic number of the α^{th} nucleus.

Because the mass of a nucleus is at least a 1000 times larger than the electron mass, it is a reasonable approximation¹ to separate the electron movement from the nucleus movement, i.e. we assume that the electrons immediately follow the movement of the nuclei. This is realized in the Born-Oppenheimer approximation[2] and we can write the total many-body state as :

$$|\Psi_{tot}\rangle = |\Psi_{at}\rangle \left| \Phi_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) \right\rangle. \quad (10)$$

In this approximation the electronic wave function only depends parametrically on the atomic positions \vec{R}_α , so the electrons instantaneously follow the atomic nuclei, and equation (3) can be separated into two equations : one describing the electronic states and one describing the atomic states.

$$\hat{H}_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) \left| \Phi_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) \right\rangle = E_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) \left| \Phi_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) \right\rangle \quad (11)$$

$$\hat{H}_{at} |\Psi_{at}\rangle = \left[E - E_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) \right] |\Psi_{at}\rangle. \quad (12)$$

The electronic and atomic Hamiltonians are given by :

$$\hat{H}_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{N-e}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) \quad (13)$$

$$\hat{H}_{at} = \hat{T}_N + \hat{V}_{N-N}, \quad (14)$$

where the electronic Hamiltonian and thus the electronic eigen equation still parametrically depend on the atomic positions through the nucleus-electron interaction. In coordination space equation (12) can be rewritten as :

$$\left[- \sum_{\alpha=1}^{N_{at}} \frac{\hbar^2}{2M_\alpha} \nabla_{\vec{R}_\alpha}^2 + V_{IAP}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) \right] \Psi_{at}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) = E \Psi_{at}(\vec{R}_1, \dots, \vec{R}_{N_{at}}), \quad (15)$$

where we defined the ‘*interatomic potential*’ as :

$$V_{IAP}(\vec{R}_1, \dots, \vec{R}_{N_{at}}) = \frac{1}{2} \sum_{\alpha, \beta} \frac{Z_\alpha Z_\beta}{|\vec{r}_\alpha - \vec{r}_\beta|} e^2 + E_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}}). \quad (16)$$

The interatomic potential $V_{IAP}(\vec{R}_1, \dots, \vec{R}_{N_{at}})$ contains the repulsive Coulomb interaction between the nuclei and all the electronic interactions through the term $E_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}})$. We conclude this section by noting that in molecular dynamics the Schrödinger equation (1) is often replaced by Newton’s equations :

$$M_\alpha \frac{d^2 \vec{R}_\alpha}{dt^2} = -\nabla_\alpha V_{IAP}(\vec{R}_1, \dots, \vec{R}_{N_{at}}), \quad \alpha = 1, \dots, N_{at}. \quad (17)$$

The rest of the underlying text will be devoted to describing useful approximations to describe the interatomic potential $V_{IAP}(\vec{R}_1, \dots, \vec{R}_{N_{at}})$.

¹Except in cases where electron-phonon interactions play an important role.

2 Interatomic potentials

In principle, the interatomic potential can be calculated by solving the electronic Schrödinger equation for the atomic positions of interest. The electronic Schrödinger equation describes the electronic many body system that can be solved using ‘*ab initio*’ techniques such as Density Functional Theory (DFT), Hartree Fock (HF), Configuration Interaction (CI), Coupled Cluster (CC), ... [3, 4]. All these types of *ab initio* techniques yield N_{el} Self-Consistent Field (SCF) equations parametrically depending on the atomic positions. The computation time for solving these SCF equations increases rapidly with the number of electrons in the system, so that these types of techniques become quickly unmanageable.

It is at this point that the semi-empirical methods come in. In these methods one essentially tries to fit the Inter Atomic Potential (IAP) to experimental or *ab initio* obtained data. In the following sections we will concentrate on the semi-empirical IAP.

2.1 Semi-empirical interatomic potentials

In the semi-empirical IAP theory, we want to expand the total energy of interatomic interaction of the N_{at} -atom system in summations over many body terms. In general we get :

$$E_{tot} = E_0 + \frac{1}{2!} \sum_{\alpha,\beta} V_2(\vec{R}_\alpha, \vec{R}_\beta) + \frac{1}{3!} \sum_{\alpha,\beta,\gamma} V_3(\vec{R}_\alpha, \vec{R}_\beta, \vec{R}_\gamma) + \dots \quad (18)$$

In this expansion E_0 represents the reference energy (and is left away in the following) and V_n represents the interatomic potential function describing the n-body interactions. When only pair interactions are included we speak of **pair potentials** and when higher order interactions are included of **cluster potentials**. Pair potentials are typically designed to model a small class of atomic rearrangements and have a small range of applicability. Cluster potentials improve on pair potentials by addition of higher order interactions. Three body and higher order terms contain information about angles between bonds, absent in pair potential descriptions. In practice cluster potentials are typically truncated at the three body level. Cluster potentials can treat a broader range of atomic configurations than a pair potential scheme, but nevertheless they are far from providing a global description of E_{tot} . The price to be paid for using cluster potentials over pair potentials is a significant increase in the computation time.

Another way to expand the total energy of interatomic interaction is like :

$$E_{tot} = E_0 + \frac{1}{2} \sum_{\alpha,\beta} V_2(\vec{R}_\alpha, \vec{R}_\beta) + \sum_{\alpha} F \left[\sum_{\beta} g_2(\vec{R}_\alpha, \vec{R}_\beta), \sum_{\beta,\gamma} g_3(\vec{R}_\alpha, \vec{R}_\beta, \vec{R}_\gamma), \dots \right]. \quad (19)$$

Instead of expressing the total energy of interatomic interaction as a sum of pair and higher order interactions, we express the higher order interactions as a *functional* F of cluster terms g_n . The energy functional F describes how the part of E_{tot} associated with atom α depends on the local environment described by the functions g_n . If the functions g_n describing the local environment are limited to pair interactions we speak of a **pair functional**. In the case where higher order interaction terms are retained we speak of **cluster functionals**. Pair functionals thus generalize pair potentials, and provide a much improved description of a broad range of inhomogeneous environments. If in addition an opportune cut-off radius is chosen, the computational speed is roughly the same as with the pair potential. In an analogue way cluster functionals generalize cluster potentials. By explicitly including angular forces in the

functions describing the local environment, cluster functionals improve on the accuracy of pair functionals and they can also handle a broader range of inhomogeneous environments than cluster potentials. The cluster functionals are typically limited to the three and four body levels, because at these levels the atomic geometries can still be visualized and the computation time is significantly shorter than for the higher order treatments.

The semi-empirical interatomic potentials can thus be divided into four main groups :

1. pair potentials
2. pair functionals
3. cluster potentials
4. cluster functionals

In the following sections we will describe some popular methods for deriving semi-empirical IAP's as well as give some commonly used parameterizations for IAP's.

2.2 Pair potentials

Since the pair potential reappears both in cluster potentials and cluster functionals, it is useful to give the explicit form of some commonly used potentials of this type.

2.2.1 Repulsive wall potentials

These kinds of potentials are used to model the repulsive part of the interaction potential that is valid at small particle separation ($< 1 \text{ \AA}$). Such types of potentials are important for modeling collision cascades of energetic particles.

A commonly used repulsive wall potential is the two body screened Coulomb potential given by :

$$V(r) = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r} \chi(x), \quad (20)$$

with $x = r/a_0$ and a_0 the the screening length defined by :

$$a_0 = 0.8853 a_B \bar{Z}^{-1/3}. \quad (21)$$

The quantity \bar{Z} is an 'average' atomic number of the two particles. The form favored by **Firsov**[5] is :

$$\bar{Z}^{-1/3} = \left(Z_1^{1/2} + Z_2^{1/2} \right)^{-2/3}, \quad (22)$$

although **Bohr**[6] used :

$$\bar{Z}^{-1/3} = \left(Z_1^{2/3} + Z_2^{2/3} \right)^{-1/2}. \quad (23)$$

Regarding this, the screening length a_0 is often used as a fitting parameter to SCF calculations or experimental data. The form of the function χ proposed by Firsov is the solution of the Thomas-Fermi equation :

$$x^{1/2} \frac{d^2 \chi}{dx^2} = \chi^{3/2}. \quad (24)$$

For the **Molière**[7], **krypton-carbon**[8] and **ZBL**[9] potentials the function χ takes the form :

$$\chi(x) = \sum_{i=1}^4 a_i e^{-b_i x}. \quad (25)$$

The **Lenz-Jenson** potential is given by :

$$\chi(x) = e^{-q} \left(1 + \sum_{i=1}^4 a_i q^i \right); \quad q = 3.11126x^{1/2}. \quad (26)$$

In all cases χ is fitted to the numerical solution of the Thomas Fermi equation, and the fitting parameters are summarized in table 1. In atomic collision studies the ZBL potential is most frequently used because of the better experimental agreement than the others.

Another frequently used form for the repulsive wall potential is the **Born-Mayer**[11] potential, which takes the form :

$$V(r) = A e^{-br}. \quad (27)$$

This potential is less satisfactory for atomic collision studies because the values A and b must be determined independently for each pair combination. Even so, it proved to be effective in order to reproduce threshold displacement energies in metals (e.g. iron)[10]. This form of the repulsive potential is mainly used to model the near-neighbor repulsion for certain ionic materials. A table with values can be found in [12].

	a_1	a_2	a_3	a_4	b_1	b_2	b_3	b_4
Molière	0.35	0.55	0.1	0	0.3	1.2	6.0	0
Krypton-carbon	0.19095	0.47367	0.33538	0	0.27854	0.63717	1.91926	0
ZBL	0.1818	0.5099	0.2802	0.02813	0.27854	0.63717	1.91926	0
Lenz-Jenson	1.0	0.3344	0.0486	0.002647				

Table 1: Numerical coefficients for screened Coulomb potentials.

2.2.2 Attractive well potentials

These types of potentials describe the attractive part of the interaction potential at particle separations of around 1-4 Å. A major drawback of these types of potentials is that they have a very limited range of applicability. For instance they can only describe close packed crystal structures. Two forms are widely used, namely the Lennard-Jones and Morse potential.

The **Lennard-Jones**[13] potential takes the form :

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (28)$$

This potential was developed to represent noble gases and is based on the premise that atoms in a solid noble gas are only slightly distorted from the stable electronic closed-shell configuration they possess in the free state. Small distortions in the electronic closed-shell configuration give rise to dipole interactions which are proportional to r^{-6} . It is these interactions that lead to the Van Der Waals forces between closed shell atoms. For short distances the electronic shells of both atoms begin to overlap, and because of the Pauli-principle a strong repulsion between

the two atoms becomes active, here taken to be proportional² to r^{12} . In this form, $2^{1/6}\sigma$ is the equilibrium spacing and ϵ the well depth. Both these parameters can be fit to *ab initio* calculations.

The **Morse**[14] potential takes the form :

$$V(r) = \frac{D_e}{S-1} \left[e^{-(2S)^{1/2}\beta(r-R_e)} - S e^{-(2/S)^{1/2}\beta(r-R_e)} \right]. \quad (29)$$

In its original form the parameter S was set to $S = 2$. The three remaining fitting parameters are the dimer energy D_e , the equilibrium displacement R_e and a parameter β , which is usually fitted to the bulk modulus of the material. In the modified form as given by (29), S is an extra fitting parameter.

2.2.3 Overlap potentials

When studying interatomic scattering in a wide energy range, such as collision cascades, one should use a potential that both describes the cohesion and bonding as well as the repulsion. A possible solution for such a situation consists in numerically merging an attractive well potential with a repulsive wall potential. In the transition zone a cubic spline can be used. In general the resulting potential should look like :

$$V(r) = \begin{cases} \text{Repulsive wall} & 0 < r < r_a \\ \text{Cubic spline} & r_a \leq r < r_b \\ \text{Attractive well} & r_b \leq r \end{cases} \quad (30)$$

There is some flexibility over the choice of r_a and r_b , but in general these are fixed at the start. Attention should be paid to the transition region, because although the cubic spline usually gives a smooth join between the potentials, in some cases it can produce oscillations in the potential curve over the joining region. These unphysical oscillations should be averted at all times, because collision cascades are often sensitive in the overlap regime.

2.3 Empirical extension of the pair potential

In this subsection we describe an *ad hoc* extension of a Morse-like potential, in order to include angular contributions to the potential, without going to the classical many-body expansion. Such an extension is given by **Tersoff**[15], who included an environment dependent bond-order, i.e. the bond-strength, explicitly into a pair potential. The potential is given as :

$$V(R_{\alpha\beta}) = f_C(R_{\alpha\beta}) [a_{\alpha\beta} f_R(R_{\alpha\beta}) + b_{\alpha\beta} f_A(R_{\alpha\beta})], \quad (31)$$

with $R_{\alpha\beta}$ the distance between atoms α and β . The function f_R represents a repulsive pair potential and f_A an attractive pair potential. The extra term f_C is merely a smooth cut-off function to limit the range of the potential. The sole novel feature is this potential is that the coefficient $b_{\alpha\beta}$ now becomes a function of the local environment. It represents a measure of the bond order and is assumed to be a monotonically decreasing function of the coordination of atoms α and β . The function $a_{\alpha\beta}$ consists solely of range-limiting terms.

²There is no physical reason for the power of 12.

For the $f_R(r)$ and $f_A(r)$ exponential functions are taken :

$$f_R(r) = A \exp(-\lambda_1 r) \quad (32)$$

$$f_A(r) = -B \exp(-\lambda_2 r). \quad (33)$$

For the cut-off function the form :

$$f_C(r) = \begin{cases} 1, & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left(\frac{\pi}{2}(r - R)/D\right), & R - D < r < R + D \\ 0, & r > R + D, \end{cases} \quad (34)$$

was chosen which has a continuous value and derivative for all r and goes from 1 to 0 in a small range around R (with R the cut-off radius). The function $b_{\alpha\beta}$, containing the angular contributions, is taken to have the following form :

$$b_{\alpha\beta} = (1 + \beta^n \zeta_{\alpha\beta}^n)^{-1/2n}, \quad (35)$$

$$\zeta_{\alpha\beta} = \sum_{\gamma \neq \alpha, \beta} f_C(R_{\alpha\beta}) g(\theta_{\alpha\beta\gamma}) \exp\left[\lambda_3^3 (R_{\alpha\beta} - R_{\alpha\gamma})^3\right], \quad (36)$$

$$g(\theta) = 1 + c^2/d^2 - c^2 / [d^2 + (h - \cos \theta)^2], \quad (37)$$

where $\theta_{\alpha\beta\gamma}$ is the bond angle between bonds $\alpha\beta$ and $\alpha\gamma$. Note that $b_{\alpha\beta} \neq b_{\beta\alpha}$. In the ‘*effective coordination*’ function $\zeta_{\alpha\beta}$ the relative distance and bonding angle of the different neighbors are taken into account. For the $a_{\alpha\beta}$ function the following form is proposed :

$$a_{\alpha\beta} = (1 + \kappa^n \eta_{\alpha\beta}^n)^{-1/2n} \quad (38)$$

$$\eta_{\alpha\beta} = \sum_{\gamma \neq \alpha, \beta} f_C(R_{\alpha\beta}) \exp\left[\lambda_3^3 (R_{\alpha\beta} - R_{\alpha\gamma})^3\right]. \quad (39)$$

In this expression κ is taken sufficiently small so that $a_{\alpha\beta} \approx 1$. These kinds of potentials were originally developed for describing semi-conductors, but have recently regained interest for the description of intermetallics.

2.4 The embedded atom method

The Embedded Atom Method (EAM) has its roots in DFT, where the Hohenberg and Kohn theorem[16] states that the total electron density uniquely determines the external potential up to an additive constant and *vice versa*. As a consequence of this theorem the Stott-Zaremba corollary[17] can be formulated as : ‘The embedding energy of an impurity is determined by the electron density of the host system before the impurity is added.’

This corollary can be understood as follows : the unperturbed host potential is determined by its electron density. When an impurity is introduced, the total potential is a sum of host and impurity potentials, so the energy of the host with impurity is a functional of the host and impurity potentials. Since the host electron density and the impurity potential are set by the position and charge of the impurity nucleus, the energy of the host with impurity is a functional of the unperturbed host electron density and a function of the impurity type and position. The total energy can be written as :

$$E = \mathcal{F}_{Z,R}[\rho_h(r)], \quad (40)$$

where $\rho_h(r)$ is the unperturbed host electron density, and Z and R are the type and position of the impurity. The functional \mathcal{F} is universal and independent of the host but its form is unknown.

A simple approximation is to assume that the energy depends only on the limited environment immediately around the impurity, or equivalently that the impurity experiences a locally uniform electron density. This approximation is known as the quasi-atom approximation[18]. This simplification can be viewed either as a local approximation or as the lowest order term involving the successive gradients of the density.

Because each atom can be viewed as an impurity in the host of other atoms, within the quasi-atom approximation the total energy can be written as :

$$E = \sum_{\alpha} F_{\alpha}[\bar{\rho}_{\alpha}], \quad (41)$$

where F is the embedding energy and $\bar{\rho}_{\alpha}$ is the uniform density of the host at the position \vec{R}_{α} without the atom α . It is important to notice that the embedding function F is not the same as the functional \mathcal{F} . The assumption of extreme locality, or complete uniformity of the electron gas and background leads to unrealistic values for (41). To correctly describe the energy, a core-core repulsion has to be added, and is here assumed to take the form of a short-range pairwise repulsion between cores.

When using a well chosen cut-off radius, the EAM energy can be evaluated in roughly the same computation time as for pair potentials. The total energy becomes :

$$E_{tot} = \frac{1}{2} \sum_{\alpha, \beta} V(R_{\alpha\beta}) + \sum_{\alpha} F[\bar{\rho}_{\alpha}], \quad (42)$$

with $F[\bar{\rho}_{\alpha}]$ the embedding functional and $\bar{\rho}_{\alpha}$ a superposition of atomic densities given by :

$$\bar{\rho}_{\alpha} = \sum_{\beta} \rho(R_{\alpha\beta}). \quad (43)$$

The atomic electron density function $\rho(R_{\alpha\beta})$ depends only on the distance between atoms α and β . Note that if the embedding functional $F[\rho]$ has the form :

$$F[\rho] = -A \rho^{1/2}, \quad (44)$$

we mathematically have the same expression as in the Tight Binding model for the Second Moment Approximation (see section 2.5). In general, the functional $F[\rho]$ has no predefined functional form. Its form is determined in the fitting procedure.

Daw and Baskes[19, 20] fitted the embedding functional as function of $\bar{\rho}_{\alpha}$ and $\rho(R_{\alpha\beta})$, with $\rho(R_{\alpha\beta})$ given as :

$$\rho(R_{\alpha\beta}) = \frac{Z_{\alpha}Z_{\beta}}{R_{\alpha\beta}} \quad Z(r) = Z_0(1 + \gamma r^{\kappa}) e^{-\nu r}, \quad (45)$$

where γ , κ and ν are adjustable parameters and Z_0 is the number of valence electrons.

In the **Voter-Chen** functional, the density function of a hydrogenic 4s orbital is taken :

$$\rho(r) = r^6(e^{-\beta r} + 2^9 e^{-2\beta r}), \quad (46)$$

while in **Foiles'** functional the density function is given by :

$$\rho(r) = r^8(e^{-\beta r} + 2^{11}e^{-2\beta r}). \quad (47)$$

For the **Johnson**[21] (analytic) functional, a universal form for the embedding functional is proposed :

$$F[\rho] = -F_0 \left[1 - n \ln \left(\frac{\rho}{\rho^{eq}} \right) \right] \left(\frac{\rho}{\rho^{eq}} \right)^n, \quad (48)$$

where ρ^{eq} is the equilibrium value of the electron density ρ . F_0 and n can be determined as :

$$F_0 = E_c - E_f \quad (49)$$

$$n = \sqrt{\frac{\Omega B}{A \beta^2 E_f}}, \quad (50)$$

where E_c is the cohesive energy per element, E_f is the monovacancy formation energy, Ω the equilibrium atomic volume, B the bulk modulus and $A = 2C_{44}/(C_{11} - C_{12})$ the anisotropic ratio. The density function is parameterized as :

$$\rho(r) = \rho_e \left(\frac{r_1}{r} \right)^\beta, \quad (51)$$

where the parameter β is taken as 6 for all bcc transition metals, and the parameter ρ_e is the value of the atomic electron density distribution at the nearest neighbor (here taken to be 1).

2.5 The tight-binding method

For the Tight Binding (TB) method, the terminology semi-empirical is well placed, because the form of the functional F in equation (19) describing the 'embedding' energy will be deduced using approximations from first principles. To come to a functional form, we first focus again on the Born-Oppenheimer approximation and solve the electronic Schrödinger equation (11) using one of the above mentioned *ab initio* techniques. These techniques reduce the electronic Schrödinger equation to N_{el} single particle SCF equations, i.e. each equation describes one electron. In this way the electronic state can be written as a linear expansion of molecular orbitals :

$$|\Phi_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}})\rangle = \sum_s a_s |\psi_s(\vec{R}_1, \dots, \vec{R}_{N_{at}})\rangle, \quad (52)$$

with s representing the Molecular Orbital (MO) and a_s the expansion coefficients. Note that in this description each MO is associated with all the atomic nuclei, in other words, the electrons are *delocalized*. Each MO is occupied by two electrons with anti-parallel spin, so the index s runs over all $N_{el}/2$ MO's.

In the TB approach, one approximates the MO as a Linear Combination of Atomic Orbitals (LCAO)³ :

$$|\psi_s(\vec{R}_1, \dots, \vec{R}_{N_{at}})\rangle = \sum_\alpha \sum_\sigma b_{\alpha\sigma}^{(s)} |\phi_\sigma(\vec{R}_\alpha)\rangle, \quad (53)$$

with σ representing an Atomic Orbital (AO) and $b_{\alpha\sigma}^{(s)}$ the expansion coefficients associated with MO s . In this approximation each electron is associated with one certain atom, in other words,

³In practice the electronic problem is first solved in the LCAO approximation, and later the MO are constructed.

the electrons are now *localized*. Each AO is occupied by two electrons with anti-parallel spin. The electronic state in the LCAO approximation now becomes :

$$\begin{aligned} |\Phi_{el}(\vec{R}_1, \dots, \vec{R}_{N_{at}})\rangle &= \sum_{\alpha} \sum_{\sigma} \left(\sum_s a_s b_{\alpha\sigma}^{(s)} \right) |\phi_{\sigma}(\vec{R}_{\alpha})\rangle \\ &= \sum_{\alpha} \sum_{\sigma} c_{\alpha\sigma} |\phi_{\sigma}(\vec{R}_{\alpha})\rangle \end{aligned} \quad (54)$$

where the index σ runs over all AO's. By solving the electronic problem in LCAO approximation we get $N_{el}/2$ different binding single particle energy levels with multiplicity two, associated with $N_{el}/2$ occupied MO's with two anti-parallel spin electrons per MO. Note that the MO's form a complete orthogonal set, while the AO's form a complete but usually non-orthogonal set. This is because the different AO's are centered above different nuclei. With the energy levels ϵ_s we can define the band energy E_{band} as the sum over all occupied energy levels :

$$E_{band} = 2 \sum_s n_s \epsilon_s, \quad (55)$$

with n_s the occupancy number of MO s , which is 1 if MO s is occupied and is 0 if MO s is unoccupied. With these results we can write the density of states (energy distribution of the MO's) as :

$$\begin{aligned} D(\epsilon) &= \sum_s \delta(\epsilon - \epsilon_s) \\ &= \sum_{\alpha\sigma} D_{\alpha\sigma}(\epsilon). \end{aligned} \quad (56)$$

In the second line we considered $D(\epsilon)$ to be the sum of the local densities of states for each AO in the system. This consideration is satisfied if the local density of states is given by :

$$D_{\alpha\sigma}(\epsilon) = \sum_s \left| \langle \psi_s(\vec{R}_1, \dots, \vec{R}_{N_{at}}) | \phi_{\sigma}(\vec{R}_{\alpha}) \rangle \right|^2 \delta(\epsilon - \epsilon_s). \quad (57)$$

In general, when atoms are brought together to form a condensed system, their energy levels become 'bands' and we can consider the band seen by each atom as described by the local density of states. We can now thus say that :

$$\begin{aligned} U_{TB}^{tot} &= 2 \sum_{\alpha,\sigma} \int_{-\infty}^{+\infty} \epsilon n(\epsilon) D_{\alpha\sigma}(\epsilon) d\epsilon \\ &= 2 \sum_{\alpha,\sigma} \int_{-\infty}^{\epsilon_F} \epsilon D_{\alpha\sigma}(\epsilon) d\epsilon \\ &= \sum_{\alpha} F_{\alpha}, \end{aligned} \quad (58)$$

with $n(\epsilon)$ the occupation probability. The last line of expression (58) is particularly useful because when using classical potentials since the total energy is almost always written as a sum over atoms, $E = \sum_{\alpha} E_{\alpha}$. Therefore, this relation is our key to establish the bridge between the quantum and classical worlds.

To obtain $D_{\alpha\sigma}(\epsilon)$ exactly, it is in principle necessary to know the positions of all the atoms in the crystal. Furthermore, $D_{\alpha\sigma}(\epsilon)$ is a very complicated functional of these positions. However, for our purposes we often do not need to calculate the detailed structure of $D_{\alpha\sigma}(\epsilon)$. To obtain

an approximate evaluation of quantities such as F_α which involves integrals over $D_{\alpha\sigma}(\epsilon)$, we need only information about its width and gross features of its shape. This information is conveniently summarized in the moments of $D_{\alpha\sigma}(\epsilon)$, defined by :

$$\mu_p^{\alpha\sigma} = \int_{-\infty}^{+\infty} \epsilon^p D_{\alpha\sigma}(\epsilon) d\epsilon. \quad (59)$$

Using equation (57) we can write :

$$\mu_p^{\alpha\sigma} = \sum_s \left| \langle \psi_s(\vec{R}_1, \dots, \vec{R}_{Nat}) | \phi_\sigma(\vec{R}_\alpha) \rangle \right|^2 \epsilon_s^p \quad (60)$$

$$\begin{aligned} &= \sum_s \langle \psi_s(\vec{R}_1, \dots, \vec{R}_{Nat}) | \phi_\sigma(\vec{R}_\alpha) \rangle \langle \phi_\sigma(\vec{R}_\alpha) | \hat{H}^p | \psi_s(\vec{R}_1, \dots, \vec{R}_{Nat}) \rangle \\ &= \langle \phi_\sigma(\vec{R}_\alpha) | \hat{H}^p | \phi_\sigma(\vec{R}_\alpha) \rangle \\ &= \sum_{\alpha_1 \sigma_1 \dots \alpha_{p-1} \sigma_{p-1}} \langle \phi_\sigma(\vec{R}_\alpha) | \hat{H} | \phi_{\sigma_1}(\vec{R}_{\alpha_1}) \rangle \dots \langle \phi_{\sigma_{p-1}}(\vec{R}_{\alpha_{p-1}}) | \hat{H} | \phi_\sigma(\vec{R}_\alpha) \rangle. \end{aligned} \quad (61)$$

So the p^{th} order moment can be evaluated by a sum over matrix elements of the TB Hamiltonian \hat{H} ⁴. Note that $\mu_0^{\alpha\sigma} = 1$ and $\mu_1^{\alpha\sigma}$ represents an average energy for the atom, related with the choice of the zero for the energy scale. The really relevant information on the shape of $D_{\alpha\sigma}(\epsilon)$ is therefore contained in $\mu_2^{\alpha\sigma}$ and higher order moments.

In the specific case of transition metals, it is believed that the properties of a transition metal is characterized by the filling of the d-band, and that for many purposes we may neglect the s- and p-electrons as a first approximation. So the density of states $D_{\alpha\sigma}(\epsilon)$ corresponding to d-orbitals can be grouped into one density of states for the d-band $D_{\alpha d}(\epsilon)$. According to this approximation only the density of states corresponding to the d-band is retained. For the sake of simplicity we will drop the orbital indexes in what follows, and in the same spirit as for transition metals we will assume that we can characterize a material by considering only one band.

If we assume the average energy is zero, the second moment is a variance and therefore represents the square of the energy width or ‘bandwidth’ of the local density of states. Higher moments describe the band shape. In the Second Moment Approximation (SMA) one gets for the total TB energy⁵ :

$$\begin{aligned} U_{TB}^{tot} &= \sum_\alpha F[\mu_2^\alpha] \quad (62) \\ &= -A \sum_\alpha (\mu_2^\alpha)^{1/2} \\ &= -A \sum_\alpha \sqrt{\sum_\beta H_{\alpha\beta}^2} \end{aligned}$$

Attempts to calculate the matrix elements by *ab initio* gave poor quantitative results. For empirical fitting, the matrix elements $H_{\alpha\beta}^2$ can be seen as cohesive potential functions describing the local environment and only depending on the interatomic distance between atom α and β . In what follows these functions are denoted as $\rho(R_{\alpha\beta})$ in analogy with the EAM and are fitted to experimental or *ab initio* data.

⁴These matrix elements are often referred to as ‘hopping integrals’, because one starts from an atom α , hops over $p - 1$ atoms to come back at atom α .

⁵Since μ_2^α is an energy variance, its square root has the dimension of energy.

In order to treat problems with TB pair functionals, it is necessary to augment the attractive electronic band energy U_{TB}^{tot} by a repulsive force which prevents the lattice from collapsing. The physics underlying this force is simply the Pauli repulsion resulting from the compression of the valence electron gas. With these notions we can write the total energy as :

$$\begin{aligned} E_{tot} &= \frac{1}{2} \sum_{\alpha,\beta} V(R_{\alpha\beta}) + \sum_{\alpha} F[\mu_2^{\alpha}] \\ &= \frac{1}{2} \sum_{\alpha,\beta} V(R_{\alpha\beta}) - A \sum_{\alpha} \sqrt{\sum_{\beta} \rho(R_{\alpha\beta})}. \end{aligned} \quad (63)$$

Justification for expressing E_{tot} as the sum of a pair potential term and a TB electronic band term has been given by the Tight Binding Bond model[22, 23].

In cases of compression of transition metals[24] or modeling of certain alloys[25], it is believed that the s-electrons as well as the d-electrons play an important role for characterizing the material. In these cases, analogue as for the d-orbitals, the s-orbitals are grouped into a s-band. In this scheme two bands are retained, yielding a total energy as :

$$E_{tot} = \frac{1}{2} \sum_{\alpha,\beta} V(R_{\alpha\beta}) + \sum_{\alpha} F_s[\mu_2^{\alpha s}] + \sum_{\alpha} F_d[\mu_2^{\alpha d}]. \quad (64)$$

This form of the SMA in TB is known as the **Two Band Model**, which can also be applied for modeling magnetism[26].

We will now discuss some frequently used TB functionals in SMA. One of the first functionals of this kind was the **Finnis-Sinclair**[27] functional⁶. For this functional both the repulsive part $V(R_{\alpha\beta})$ and the cohesive part $\rho(R_{\alpha\beta})$ were assumed to be short-ranged and were parameterized to fit the lattice constant, cohesive energy and all three elastic moduli of the seven bcc transition metals. For the cohesive potential $\rho(r)$ the parabolic form was adopted given by :

$$\rho(r) = (r - d)^2 \theta(d - r), \quad (65)$$

while for the pair potential $V(r)$ a quartic polynomial form was adopted given by :

$$V(r) = (r - c)^2 (c_0 + c_1 r + c_2 r^2) \theta(c - r) \quad (66)$$

The parameters d and c are cut-off radii and are assumed to lie between the second and third nearest neighbors. The three parameters c_0 , c_1 and c_2 together with A are used for fitting the experimental data. This functional can account for experimental vacancy formation energies and does not require an externally applied pressure to balance the ‘Cauchy pressure’.

A functional of the same type was developed by **Ackland**[28, 29] to describe fcc, bcc and hcp metals. For the fcc and hcp metals the potentials take the cubic form :

$$V(r) = \sum_{k=1}^6 a_k (r_k - r)^3 \theta(r_k - r), \quad r_1 > r_2 \dots > r_6, \quad (67)$$

$$\rho(r) = \sum_{k=1}^2 A_k (R_k - r)^3 \theta(R_k - r), \quad R_1 > R_2. \quad (68)$$

The parameters r_1 and R_1 represent the cut-off radii for V and ρ and all the other parameters are used for fitting to experimental data, usually the lattice constant, cohesive energy, the

⁶In general TB functionals in SMA are often referred to as Finnis-Sinclair (FS) functionals.

elastic constants C_{11} , C_{12} and C_{44} and the Cauchy pressure. Note that in this form the global scaling factor A is left away and replaced by two independent scaling factors A_k . For the bcc lattice the above form was modified to the **Ackland-Thetford**[30] functional, given by :

$$\rho(r) = \theta(d-r)(r-d)^2 \quad (69)$$

$$V_2(r) = \theta(c-r)(r-c)^2(c_0 + c_1r + c_2r^2) + B\theta(b_0-r)(b_0-r)^3 e^{-\alpha r}. \quad (70)$$

Traditionally, the SMA has been applied to both fcc and bcc metals, while EAM has been applied predominantly to fcc metals. There is no particular reason to view either approach as better suited for either crystal type, although the restriction that F be a negative square root presumably makes the SMA less flexible. An appealing aspect of the second moment view of EAM is that it offers a natural pathway to more accurate potentials. By extending the energy expression to include higher moments, either via the recursion method[31, 32] or other approaches[33], the intricacies of chemical bonding are more faithfully represented. Higher moments are simply formed from Hamiltonian products that correspond to paths with more atom to atom jumps. A comparison between the two methods is presented in table 2.

	TB	EAM
Environmental parameter	Squared bandwidth μ_2^α	Local electron density $\bar{\rho}_\alpha$
Pair assumption	$\mu_2^\alpha = \sum_\beta \rho(R_{\alpha\beta})$	$\bar{\rho}_\alpha = \sum_\beta \rho(R_{\alpha\beta})$
Functional form	$-A(\mu_2^\alpha)^{1/2}$	Numerically determined
Higher order expansion	$F[\mu_2^\alpha, \mu_3^\alpha, \dots]$	$F[\rho_\alpha, \nabla\rho_\alpha]$
Function to be fitted	μ_2^α	$F[\bar{\rho}_\alpha]$

Table 2: Comparison between SMA in the TB method and the EAM.

3 Empirical extensions on TB and EAM

In the literature a lot of *ad hoc* modification and extensions on the EAM and TB method can be found. In all cases these extensions are necessary to increase the number of free parameters for fitting extra material characteristics, which are incompatible in the EAM and TB framework. In the following some successful modifications are summarized.

3.1 The modified embedded atom method

The Modified Embedded Atom Method (MEAM) is an empirical extension on the EAM, originally designed to reproduce the elastic constants of all the transition metals, even the ones with negative Cauchy pressures (such as Cr). The idea behind the MEAM is to include bond angles, which are not described in the EAM, because the atomic electron densities are taken spherically symmetric. The EAM can be modified in two ways :

1. Leave the functional form of the EAM the same, and augment the spherically symmetric atomic electron densities by angularly dependent terms.[34, 35, 36, 37]
2. Keep the electronic density unchanged, but add a modified energy term to the total energy expression.[38, 39]

For the first option the expression for the total energy E_{tot} stays the same as in (42) :

$$E_{tot} = \frac{1}{2} \sum_{\alpha,\beta} V(R_{\alpha\beta}) + \sum_{\alpha} F[\bar{\rho}_{\alpha}], \quad (71)$$

but the average atomic densities $\bar{\rho}_{\alpha}$ are modified as :

$$\bar{\rho}_{\alpha} = \rho_{\alpha}^{(0)} + \rho_{\alpha}^{(1)} + \rho_{\alpha}^{(2)} + \rho_{\alpha}^{(3)}. \quad (72)$$

In this expression the first term is the spherically symmetric partial electron density (the same as the EAM electron density), and the following three terms are the angular contributions. Different explicit expressions for the angular contributions can be found in [34, 36, 40].

For the second option the atomic electronic density stays unchanged, but in the total energy expression a modified energy term is added to express the difference between the actual total energy of the system and the calculated energy from EAM, using a linear superposition of spherically symmetric atomic electron densities.

$$E_{tot} = \frac{1}{2} \sum_{\alpha,\beta} V(R_{\alpha\beta}) + \sum_{\alpha} F[\bar{\rho}_{\alpha}] + \sum_{\alpha} M[P_{\alpha}], \quad (73)$$

with :

$$P_{\alpha} = \sum_{\beta} \rho(R_{\alpha\beta})^2. \quad (74)$$

The modification term is usually taken to be an exponential function and is given by[38] :

$$M[P] = \kappa \left(\frac{P}{P_e} - 1 \right)^2 \exp \left[- \left(\frac{P}{P_e} - 1 \right)^2 \right], \quad (75)$$

with :

$$\kappa = \frac{n^2 F_0}{8} + \frac{9\Omega B - 15\Omega G}{8\beta^2}. \quad (76)$$

In this expression the same notation as for the Johnson functional (see section 2.4) was used. The constant P_e is the argument of the modification term taken an equilibrium of the electron density and the constant $G = (3C + 2C')/5$ is the Voigt average shear modulus with $C = C_{44}$ and $C' = (C_{11} - C_{12})/2$.

3.2 The embedded defect method

The Embedded Defect Method (EDM) is an extension to the EAM, in a quite analogue way as the MEAM. The EDM was originally developed for the same reasons as the MEAM, to describe the elastic constants of transition metals, in particular the elements that have a negative Cauchy pressure, and is very useful for simulations of defects in transition metals.

The formalism of the EDM is built to incorporate angular dependent densities in the EAM. Essentially, instead of computing the electronic density at every atom site, the ‘*dipole electron density tensor*’ is calculated, given by :

$$\bar{\bar{\lambda}}_{\alpha} = \sum_{\beta} \rho(R_{\alpha\beta}) (\vec{r}_{\alpha\beta} \otimes \vec{r}_{\alpha\beta}), \quad (77)$$

with $\vec{r}_{\alpha\beta}$ the unit vector joining atom α and atom β . The symbol \otimes denotes the tensor product. This tensor can be separated into an isotropic \bar{S} and so called deviatoric tensor \bar{D} (trace null). The trace of the isotropic tensor corresponds to an invariant of $\bar{\lambda}$ and is nothing more than one third of the average atomic electronic density $\bar{\rho}$ of the EAM. A second invariant of $\bar{\lambda}$ is the norm of the deviatoric tensor, which is angular dependent. This norm is given as :

$$Y_\alpha = \sum_{i,j} D_\alpha^{ij} D_\alpha^{ij}. \quad (78)$$

Within this framework, the many-body terms of the potential are two functionals F and G of these two invariants (the energy must be an invariant), the first one being nothing more than the traditional embedding function and the second one the additional non-central interaction term :

$$E_{tot} = \frac{1}{2} \sum_{\alpha,\beta} V(\vec{R}_\alpha, \vec{R}_\beta) + \sum_\alpha F[\bar{\rho}_\alpha] + \sum_\alpha G[Y_\alpha]. \quad (79)$$

As used by Pasianot *et al* [41], the functional G is a linear function through the origin for the angular term, with $G' > 0$. In this way the EDM can be considered as a first order expansion of the EAM with respect to a many body angular term Y .

3.3 Ackland-Mendelev extension to TB

This fully empirical extension on the SMA of the TB method is optimized for describing point defect interactions and compression data. The extended form of the SMA functional proposed by **Ackland-Mendelev**[42, 43] is given by :

$$F[\rho] = -A_1\sqrt{\rho} + A_2\rho^2 + A_3\rho^4. \quad (80)$$

This form for F incorporates the kinetic energy effect, taking us smoothly between hopping and free-electron dominated regimes for increasing ρ . In this framework the isotropic compression is dealt with by the many body term (high ρ), while the short atom-atom distances are addressed with a pair potential.

4 Effective potentials

Pair functionals as in the TB method or in the EAM are highly nonlinear functionals of the local environment parameter μ_2^α or $\bar{\rho}_\alpha$. The effective potential theory provides a tool for expanding such functionals in a polynomial functional of the local environment parameter. In this way a polynomial functional of the local environment parameter of the order p , yields an expansion of the energy in terms of many-body potentials up to p -body interactions. This method is for example used to expand an EAM functional in cluster terms, useful in the Cluster Variational Method (CVM).

As an example we give the expansion for the EAM, which is completely analogue to the SMA in the TB scheme. We take ρ^{ref} to be the reference environment, i.e. a particular (possibly hypothetical) environment from which the various local environments do not vary drastically, for example the electronic equilibrium density. For a suitable reference environment, we can make a Taylor expansion of the embedding functional as :

$$F[\bar{\rho}_\alpha] = F[\rho^{ref}] + \left. \frac{\delta F}{\delta \rho} \right|_{\rho=\rho^{ref}} (\bar{\rho}_\alpha - \rho^{ref}) + \frac{1}{2} \left. \frac{\delta^2 F}{\delta \rho^2} \right|_{\rho=\rho^{ref}} (\bar{\rho}_\alpha - \rho^{ref})^2 + \dots \quad (81)$$

If we retain only the linear terms, we can write the total energy E_{tot} as :

$$E_{tot} = \tilde{E}_0 + \frac{1}{2} \sum_{\alpha, \beta} V^{eff}(\vec{R}_\alpha, \vec{R}_\beta; \rho^{ref}). \quad (82)$$

In this expression the constant term and effective pair potential are given by :

$$\tilde{E}_0 = E_0 + \sum_{\alpha} \left(F[\rho^{ref}] - \rho^{ref} \left. \frac{\delta F}{\delta \rho} \right|_{\rho=\rho^{ref}} \right) \quad (83)$$

$$V^{eff}(\vec{R}_\alpha, \vec{R}_\beta; \rho^{ref}) = V(R_{\alpha\beta}) + 2\bar{\rho}_\alpha \left. \frac{\delta F}{\delta \rho} \right|_{\rho=\rho^{ref}}. \quad (84)$$

It is easy to see that retaining higher order terms in (81) will lead to cluster many-body potentials in the energy expansion. An analogue method can be applied to cluster functionals, where one has to use a multi-dimensional Taylor expansion.

5 Extension to alloys

In this section we will extend the above theory to multi-component systems. For an ordered alloy, or any system with more than one type of atom, the EAM energy expression in equation (42) is rewritten as :

$$E_{tot} = \frac{1}{2} \sum_{\alpha, \beta} V_{t_\alpha t_\beta}(R_{\alpha\beta}) + \sum_{\alpha} F_{t_\alpha}[\bar{\rho}_\alpha], \quad (85)$$

with

$$\bar{\rho}_\alpha = \sum_{\beta} \rho_{t_\beta}(R_{\alpha\beta}). \quad (86)$$

Note that the pair potential now depends on the type t_α of atom α and the type t_β of atom β , while the terms in the sum of $\bar{\rho}_\alpha$ each depend on the type of neighbor atom β . This is because the change of energy by embedding an atom into a host system is a functional of the electronic density of the host system before the new atom is embedded. Thus the average electronic density of the host system $\bar{\rho}_\alpha$ at site α is independent of the atom type to be embedded at site α . Summarized, for a binary alloy with atom types A and B , the complete EAM energy expression requires definitions for V_{AA} , V_{AB} , V_{BB} , $\rho_A(r)$, $\rho_B(r)$, $F_A[\bar{\rho}]$ and $F_B[\bar{\rho}]$. The most difficult entity to calculate will be the mixed pair potential V_{AB} , which is usually taken to be some sort of average between V_{AA} and V_{BB} .

An example of a EAM applied to a binary alloy is the **Ludwig-Farkas**[44] functional for Fe-Cu. For the mixed pair interaction potential the following form was used :

$$V_{FeCu}^{eff}(a + bx) = A \left[V_{Fe}^{eff}(c + dx) + V_{Cu}^{eff}(e + fx) \right], \quad (87)$$

where x takes values from zero to unity. The parameters a , b , c , d , e , f and A were adjusted to give a good overall fit to : (1) The vacancy-Cu binding energy in the α -Fe matrix, (2) the energy of solution of one Cu atom in the α -Fe matrix and (3) the kinetic binding energy between two Cu atoms in the α -Fe matrix defined by Osetsky and Serra[45].

Within the SMA of the TB method, the energy E_{tot} can be written as :

$$E_{tot} = \frac{1}{2} \sum_{\alpha, \beta} V_{t_\alpha t_\beta}(R_{\alpha\beta}) - \sum_{\alpha} \left(\sum_{\beta} \rho_{t_\alpha t_\beta}(R_{\alpha\beta}) \right)^{1/2}. \quad (88)$$

Note that there is actually a slight formal difference between EAM and SMA arising from the difference in their physical origins. In EAM, the terms in the density sum for atom α in equation (86) depend on the atom type of neighbor β but not on the type of atom α . This is because the fixed density on atom β is independent of atom α . In the corresponding SMA expression, the terms have a different meaning : they are the squares of matrix elements between atom α and atom β . In constructing a binary alloy potential, the SMA thus requires one more function ($\rho_{t_\alpha t_\beta}(r)$) than the EAM.

An example of the SMA in TB method, applied to a binary alloy is the **Ackland-Bacon**[46] functional for FeCu. The mixed pair potential was parameterized in the following way :

$$V_{AB}(r) = \sum_{k=1}^6 a_k^{AB} \theta(r_k^{AB} - r) (r_k^{AB} - r)^3, \quad (89)$$

and fitted at the heat of solution per atom, which is, for dilute solutions, the single substitutional impurity (SSI) energy. As fitting data the unrelaxed SSI of copper in iron and iron in copper was used. For the cross potential $\rho_{AB}(r)$ the geometric mean of the potentials for the pure elements was used :

$$\rho_{AB}(r) = \sqrt{\rho_{AA}(r)\rho_{BB}(r)}. \quad (90)$$

6 Symmetries

In the EAM as well as in the SMA in the TB model for pure elements, there are two transformations that leave the atomic site energy and thus total energy invariant. Such transformations are called *symmetries*.

For the atomic site α the energy is given as :

$$E_\alpha = \frac{1}{2} \sum_{\beta \neq \alpha} V(R_{\alpha\beta}) + F[\bar{\rho}_\alpha], \quad (91)$$

with

$$\bar{\rho}_\alpha = \sum_{\beta \neq \alpha} \rho(R_{\alpha\beta}). \quad (92)$$

It is easily verified that the transformations :

$$\begin{cases} \tilde{\rho}(R_{\alpha\beta}) &= S \rho(R_{\alpha\beta}) \\ \tilde{F}[\bar{\rho}_\alpha] &= F[\bar{\rho}_\alpha/S], \end{cases} \quad (93)$$

and

$$\begin{cases} \tilde{F}[\bar{\rho}_\alpha] &= F[\bar{\rho}_\alpha] + C \bar{\rho}_\alpha \\ \tilde{V}(R_{\alpha\beta}) &= V(R_{\alpha\beta}) - 2C\rho(R_{\alpha\beta}), \end{cases} \quad (94)$$

with S and C constants, leave the atomic site energy E_α invariant. It is important to notice that these transformations are no symmetries of the alloy energies. Since these transformations change the alloy energy without effecting the pure element energy, they can be used in the fitting procedure to improve the quality of the alloy potential.

Another important consequence of these two symmetries is that neither the pair potential V , nor the embedding functional F and neither the electron density ρ are uniquely determined. To uniquely determine the pair potential, embedding function and electronic density, two *gauge* conditions are needed : one for each symmetry.

An example of a gauge is the *effective gauge* :

1. The first condition is that derivative of the embedding functional for equilibrium density $\bar{\rho}_{eq}$ (i.e. the density for the perfect lattice) :

$$F'[\bar{\rho}_{eq}] = 0. \quad (95)$$

This condition can be easily imposed for an arbitrary functional form by the transformation (94) with $C = -F'[\bar{\rho}_{eq}]$.

2. The second condition is to normalize the total equilibrium density $\bar{\rho}_{eq}$ to one :

$$\bar{\rho}_{eq} = 1. \quad (96)$$

This condition can easily be imposed by the transformation (93) with $S = 1/\bar{\rho}_{eq}$.

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