Ab initio INTERLAYER POTENTIALS

FOR METALS AND ALLOYS

FUYANG TIAN

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Abstract

Many modern materials and material systems are layered. The properties related to layers are connected to interactions between atomic layers. In the present thesis, we introduce the interlayer potential (ILP), a novel model potential which fully describes the interaction between layers. The ILPs are different from the usual interatomic potentials which present interaction between atoms. We use the Chen-Möbius inversion method to extract the ILPs from \textit{ab initio} total energy calculations. The so obtained ILPs can be employed to investigate several physical parameters connected with the particular set of atomic layers, e.g. surface energy, stacking fault energy, elastic parameters, etc.

The interactions between the face centered cubic (fcc) (111) planes are described by two different ILPs. Using two close-packed model structures, namely the ABC stacking along the fcc \textit{⟨111⟩} direction and AB stacking along the hcp \textit{⟨0001⟩} direction, we demonstrate how these two ILPs are obtained via the Chen-Möbius method. Density function theory (DFT) is employed to generate the ILPs and also to compute the equilibrium structural properties of elemental metals Al, Ni, Cu, Ag, Au and Pd as well as of Pd-Ag random solid solutions.

With the so established ILPs, we adopt the supercell method and the axial interaction model to calculate the stacking fault energy along the fcc \textit{⟨111⟩} direction, including the intrinsic stacking fault energy, extrinsic stacking fault energy and twin stacking fault energy as well as the interactions between the intrinsic stacking faults. We find that the data derived from ILPs are consistent with those obtained in direct \textit{ab initio} calculations. Along the fcc \textit{⟨111⟩} direction, we study the surface energy and surface relaxation using the ILPs. The phonon dispersions are also described.

We conclude that the interlayer potentials based on the Chen-Möbius inversion technique may provide a new way to investigate the properties related to layers in layered materials.
Preface

List of included publications:

I A novel potential: the interlayer potential for the fcc (111) plane family

II Interlayer potentials for fcc (111) planes of Pd-Ag random alloys

Comment on my own contribution

The first publication contains results obtained during my learning project about the Chen-Möbius inversion. All calculations and data analysis in this work were done by me and the manuscript was written jointly (my contribution was about 50%).

In my second publication, which presents an application of the Chen-Möbius technique to study engineering properties of alloys, the calculations (90%), data analysis (80%) and writing (75%) were done mostly by me.

Publications not included in the thesis:

I Ab initio investigation of high entropy alloys of 3d elements

II Designing high entropy alloys with optimal properties
Lajos Varga, Fuyang Tian, and Levente Vitos, in manuscript.
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Chapter 1

Introduction

Density functional theory (DFT) [1, 2], as a powerful ground state theory, has been widely applied to investigate the structural and electronic properties of solids. However, the application of DFT to study thermodynamical behavior of realistic materials is usually accompanied by a heavy increase of the computational effort. On the other hand, model potentials, derived from experimental or \textit{ab initio} data, may be used to simulate large systems and are usually implemented in classic molecular dynamics. These potentials make relatively easy to investigate systems containing thousands of atoms and enable one to determine the trends of essential physical properties. Often by model potentials we mean interatomic interactions. In this work, we introduce a new type of potential, namely the interlayer potential (ILP) that describes the interaction between atomic layers.

Materials are composed of many atoms with ordered or disorder arrangements. In fact many modern materials and material systems are layered. The properties related to layers are derived from the interaction between layers. The interactions between the atomic layers are usually different from those within the layers and describe the layered character of the material. As a typical example, graphite is composed of hexagonal carbon sheets. The interlayer bonding properties have widely been studied [3, 4, 5, 6, 7, 8]. In ordered crystals, there may be a multiple of (up to infinite) of distinct lattice planes with different directions. For example, slip planes are \{110\} in body-center cubic (bcc) metals, \{111\} in face-center cubic (fcc) metals, and \{0001\} in hexagonal metals, respectively. Many material properties have some connections with the lattice planes, such as stacking fault energy ($\gamma_{sf}$), surface energy ($\gamma_s$), and interfacial coherent energy on different lattice planes. Therefore, the lattice planes are very crucial in the description of material properties. We consider herein each lattice plane as a unity and investigate the interaction between layers. The proposed interlayer pair potential transforms the three-dimensional structure into an one-dimensional chain and thus decreases the complexity of the many-body interaction. The ILPs can easily be applied to discuss some material properties associated with lattice planes.
The interatomic potential is of primary importance for the molecular dynamics simulations. Still, it is extremely difficult to get reliable interatomic potentials, which prevents that the interatomic potentials are applied to complex alloys. Considering the advantage of the present model potentials, we make an attempt to derive the interaction potentials between close-packed lattice planes of disordered alloys.

In order to obtain the ILPs for metals and random alloys, here we employ the Chen-Möbius inversion method \[9\]. Previously, the Chen-Möbius inversion has successfully been applied to extract the interatomic potentials from \textit{ab initio} calculations for rare earth-transition intermetallic compounds \[10\], ionic crystals \[11\], compound semiconductors \[12\], transition metal carbides or nitrides \[13, 14\] and metal/ceramic interfaces \[15\] as well as metal/SiC interface \[16\]. Recently, Yuan et al. proposed the lattice-inversion embedded-atom-method (LI-EAM) with Chen-Möbius inversion method and improved effectively the embedded-atom-method (EAM) potentials of metals \[17\]. The detailed construction of the ILPs can be found in Chapter 2.

Although one can in principle extract the model potentials from the experiments, such data are usually obtained at different experimental conditions and thus includes some degree of uncertainty. On the other hand, modern \textit{ab initio} calculations can provide total energies for complex alloys and thus can be used to derive reliable ILPs. In the present thesis, we use the CASTEP and the exact muffin-tin orbital (EMTO) computational tools to obtain the interlayer energy versus the interlayer distance for metals and alloys. The EMTO method combined with the coherent potential approximation (CPA) is considered to be a powerful tool to study random alloys and thus offers us opportunity to construct accurate ILPs for complex solid solutions. The \textit{ab initio} theory is briefly described in Chapter 3.

In fcc metals and alloys, there are several physical properties associated with the fcc (111) planes, such as the elastic constant \(C_{44}\), stacking fault energy \(\gamma_{sf}\), and surface energy \(\gamma_s\) or the phonon dispersion, which are all basic and important quantities in materials science. We describe these physical properties using the ILPs in Chapter 5.

In Chapter 6, taking pure metals Al, Ni, Cu, Ag, Au and Pd as well as random alloy Pd-Ag as examples, we discuss the properties related to layers, including the stacking fault energy (intrinsic fault, extrinsic stacking fault and twin fault), the interaction between two intrinsic stacking faults, surface energy and surface relaxations, and the phonon dispersion.
Chapter 2

Chen-Möbius inversion

Within the theory of effective interaction potentials, the energy of different structural models is usually expressed in terms of the model potentials. If the energy of a structural model is obtained by \textit{ab initio} calculations or experiments, one can use different methods to derive the model potentials. The Chen-Möbius inversion \cite{9} is an efficient and accurate tool to obtain the model potentials. The Möbius inversion \(\mu(d)\) is defined in number theory. For the sum function

\[ F(n) = \sum_{d|n} f(d), \]  

(2.1)

where \(d|n\) shows that \(d\) is a divisor of \(n\), if \(f(d)\) and \(F(n)\) satisfy

\[ f(n) = \sum_{d|n} \mu(d) F(n/d), \]  

(2.2)

then \(\mu(d)\) can be equal to

\[ \mu(d) = \begin{cases} 
1 & d = 1, \\
(-1)^r & d \text{ has } r \text{ distinct prime divisors}, \\
0 & \text{others}. 
\end{cases} \]  

(2.3)

2.1 Definition of the interlayer potentials

Before defining the interlayer potentials (ILPs), we introduce the structural models which are often used to derive the interactions between close-packed atomic layers. These models are usually based on common close-packed layered arrangements such as the fcc (111), hcp (0001) and dhcp (0001) structures shown in Figure 2.1. The stacking sequence for the fcc (111) layers is \(\cdots\text{ABCABC}\cdots\), for the hcp (0001) layers \(\cdots\text{ABAB}\cdots\),
and for the dhcp (0001) layers \( \cdots \) ABACABAC \( \cdots \). By the ABC structural model we mean a stacking sequence as in the case of the fcc (111) lattice and with the interlayer distance as the only free lattice parameter. Similarly, the structural models AB and ABAC correspond to the hcp (0001) and dhcp (0001) lattices with variable interlayer distances. For the ABC model, the ILPs are denoted by \( \phi_{AB}, \phi_{BC}, \phi_{CA}, \phi_{AC}, \phi_{BA}, \phi_{CB}, \phi_{AA}, \phi_{BB}, \) and \( \phi_{CC} \). Similarly, the potentials are \( \phi_{AB}, \phi_{BA}, \phi_{AA}, \phi_{BB} \) in the AB structural model, and \( \phi_{AB}, \phi_{BA}, \phi_{AC}, \phi_{CA}, \phi_{BC}, \phi_{CB}, \phi_{AA}, \phi_{BB}, \) and \( \phi_{CC} \) in the ABAC structural model. Due to the symmetry, we have \( \phi_{AB}=\phi_{BC}=\phi_{CA}, \phi_{AC}=\phi_{BA}=\phi_{CB}, \) and \( \phi_{AA}=\phi_{BB}=\phi_{CC} \).

By definition, the ILP \( \phi_{ab}(d) \) is between neighboring layers, i.e. between the A-B, A-C and B-C layers, and \( \phi_{aa}(d) \) between aligned layers, i.e. between the A-A, B-B and C-C layers. Here \( d \) represents the coordinate perpendicular to the layers.

### 2.2 Process of inversion

In terms of the ILPs \( \phi_{ab} \) and \( \phi_{aa} \), the total energy of the ABC structural model is given by

\[
E^{ABC}(d) = \sum_{n=1}^{\infty} 3(\phi_{ab}((3n-2)d) + \phi_{ab}((3n-1)d) + \phi_{aa}(3nd)),
\]

where \( d \) is the interlayer distance (separation between adjacent atomic layers) and the energy is per 3 atoms. For the AB and ABAC models, the corresponding total energy (per 2 and 4 atoms, respectively) may be written in the following forms.
2.2. PROCESS OF INVERSION

\[ E^{AB}(d) = \sum_{n=1}^{\infty} 2(\phi_{ab}((2n - 1)d) + \phi_{aa}(2nd)) \]  \hspace{1cm} (2.5)

and

\[ E^{ABAC}(d) = \sum_{n=1}^{\infty} (4\phi_{ab}((2n - 1)d) + 2\phi_{ab}((4n - 2)d) + 2\phi_{aa}((4n - 2)d) + 4\phi_{aa}(4nd)) . \]  \hspace{1cm} (2.6)

In the present thesis, we only use the ABC and AB structures as the calculation models for the ILPs inversion.

We can solve \( \phi_{ab} \) and \( \phi_{aa} \) if \( E^{ABC} \) and \( E^{AB} \) are known. The energy difference \( \Delta_{ab}(d) \) is defined as

\[ \Delta_{ab}(d) = E^{ABC}(d) - E^{AB}(\frac{3}{2}d), \]  \hspace{1cm} (2.7)

then we obtain two following formulas

\[ \Delta_{ab}(d) = \sum_{n=1}^{\infty} \phi_{ab}((3n - 2)d) - \sum_{n=1}^{\infty} \phi_{ab}((3n - \frac{3}{2})d) + \sum_{n=1}^{\infty} \phi_{ab}((3n - 1)d), \]  \hspace{1cm} (2.8)

or

\[ \Delta_{ab}(d) = \sum_{n=1}^{\infty} r(n)\phi_{ab}(b(n)d). \]  \hspace{1cm} (2.9)

In Table 2.1, we list the data of \( b(n) \) and \( r(n) \).

| \hline \n | 1 2 3 4 5 6 7 8 9 10 & \ldots \n \hline \n \midrule \n b(n) & 1 \frac{3}{2} 2 4 \frac{9}{2} 5 7 \frac{15}{2} 8 10 \ldots \n \hline \n r(n) & 1 -1 1 -1 1 1 -1 1 1 \ldots \n \hline

Table 2.1. The data list for the coefficients \( b(n) \) and \( r(n) \) Eq. 2.9.

By extending \( \{b(n)\} \), we construct a multiplicative semi-group \( \{B(n)\} \) as in Ref. [9]. Then it follows that

\[ \Delta_{ab}(d) = \sum_{n=1}^{\infty} R(n)\phi_{ab}(B(n)d). \]  \hspace{1cm} (2.10)

The coefficients \( R(n) \) satisfy
\[ R(n) = \begin{cases} r(b^{-1}[B(n)]) & \text{if } B(n) \in b(n), \\ 0 & \text{if } B(n) \notin b(n). \end{cases} \] \tag{2.11}

According to Chen-Möbius inversion method [9], we can get
\[ \phi_{ab}(d) = \sum_{n=1}^{\infty} J(n) \Delta_{ab}(B(n)d), \] \tag{2.12}
where \( J(n) \) satisfy
\[ \sum_{B(n)B(k)} J(n) R(B^{-1}(\frac{B(k)}{B(n)})) = \delta_{k,1}. \] \tag{2.13}

The coefficients \( B(n), R(n) \) and \( J(n) \) are listed in Table 2.2.

**Table 2.2.** The data list for the coefficients \( B(n), R(n) \) and \( J(n) \) in Eq. 2.13.

<table>
<thead>
<tr>
<th>( n )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>\ldots</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B(n) )</td>
<td>1</td>
<td>\frac{3}{2}</td>
<td>2</td>
<td>\frac{9}{4}</td>
<td>3</td>
<td>\frac{27}{8}</td>
<td>4</td>
<td>\frac{81}{16}</td>
<td>5</td>
<td>\frac{243}{32}</td>
<td>\ldots</td>
</tr>
<tr>
<td>( R(n) )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>\ldots</td>
</tr>
<tr>
<td>( J(n) )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-2</td>
<td>1</td>
<td>0</td>
<td>-2</td>
<td>-1</td>
<td>1</td>
<td>\ldots</td>
</tr>
</tbody>
</table>

Similarly, in order to solve \( \phi_{aa} \), we define
\[ \Delta'_{aa}(d) = E^{AB} \left( \frac{d}{2} \right) - \sum_{n=1}^{\infty} \phi_{ab}((n - \frac{1}{2})d), \] \tag{2.14}
then we can obtain
\[ \phi_{aa}(d) = \sum_{n=1}^{\infty} \mu(n) \Delta'_{aa}(nd), \] \tag{2.15}
in which \( \mu(n) \) satisfy
\[ \mu(n) = \begin{cases} 1 & n = 1, \\ (-1)^s & n = p_1p_2 \ldots p_s \ (p_1 \neq p_2 \neq \ldots \neq p_s), \\ 0 & \text{others}. \end{cases} \] \tag{2.16}

Apparently, the interlayer interactions can strictly be considered up to arbitrary-distance neighboring layers on the basis of Chen-Möbius inversion method. According to Eqs. 2.5 and 2.15, the premise conditions of getting \( \phi_{ab} \) and \( \phi_{aa} \) are to obtain the energy \( E^{ABC} \) and \( E^{AB} \) as a function of \( d \).
Table 2.3. The coefficient list of $\mu$ in Eq. 2.16.

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>$\cdots$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu(n)$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
Chapter 3

Ab initio theory

3.1 Density Functional Theory

Today, density functional theory \[1, 2\] is extensively applied to calculate the electronic properties of molecules and solids. The two theorems behind of density functional theory \[1\] are:

- the ground state of an interacting electron system is uniquely described by an energy functional \( E_n \) of the electron density.
- the true ground state electron density \( n(r) \) minimizes the energy functional \( E_n \) and the minimum gives the total energy.

Within the Kohn-Sham method \[2\], the total energy of a system of electrons is given as:

\[
E_{\text{tot}} = T_s + \int v_{\text{ext}}(r)n(r)d^3r + \frac{1}{2} \int \int \frac{n(r)n(r')}{|r-r'|}d^3rd^3r' + V_{\text{nn}} + E_{\text{xc}},
\]

(3.1)

where \( T_s \) is the kinetic energy of a system of noninteracting electrons, the three middle terms represent the electron-nucleus, electron-electron, nucleus-nucleus electrostatic energies, and the last term \( E_{\text{xc}} \) is the exchange-correlation energy which can be decomposed into its exchange and correlation parts \( (E_{\text{xc}}=E_x+E_c) \). The corresponding exchange-correlation potential is defined as

\[
\mu_{\text{xc}} \equiv \delta E_{\text{xc}}[n(r)]/\delta n(r).
\]

(3.2)

The Kohn-Sham equation is written as

\[
[-\nabla^2 + V_{\text{eff}}(r)]\psi_i^k = \epsilon_i^k \psi_i^k,
\]

(3.3)
3.1. DENSITY FUNCTIONAL THEORY

where

\[ V_{\text{eff}}(r) = V_{\text{ext}}(r) + \frac{1}{4\pi\epsilon_0} \int \frac{n(r')}{|r - r'|} dr' + \mu_{xc}(r), \]  

(3.4)

\( \epsilon^k_i \) are the one electron energies and \( \psi^k_i \) the corresponding Kohn-Sham orbitals. For solving Eq. 3.3 one can use fully-relativistic, scalar-relativistic or non-relativistic techniques. Because the exact form of \( \mu_{xc} \) is not known, we have to adopt different approximations. The local density approximation (LDA) [18] and the generalized gradient approximation (GGA) [19] are two most widely applied approximations for the exchange-correlation terms. There are several methods for solving the Kohn-Sham equations. Those used in the present thesis are the all-electron muffin-tin method and the pseudopotential method.

In our work, we use the CASTEP and the EMTO computational tools. In following sections, we introduce the two versions of GGA (Perdew-Burke-Ernzerhof (PBE) [19] and PBEsol [20]), the ultrasoft pseudopotentials (USP) and the exact muffin-tin orbital (EMTO) method.

### 3.1.1 Exchange-Correlation Approximations

In the local density approximation (LDA), the exchange-correlation energy is written as

\[ E_{\text{xc}}^{\text{LDA}}(n) = \int n(r) \epsilon_{\text{xc}}^{\text{LDA}}(n(r)) d^3r, \]  

(3.5)

where \( \epsilon_{\text{xc}}^{\text{LDA}} = \epsilon_x^{\text{LDA}} + \epsilon_c^{\text{LDA}} \), in which, \( \epsilon_{\text{xc}}^{\text{LDA}} \) is the exchange-correlation energy of homogeneous electron system expressed per electron, \( \epsilon_x^{\text{LDA}} \) is the exchange energy per electron and \( \epsilon_c^{\text{LDA}} \) is the correlation energy per electron.

In order to better describe an inhomogeneous system, the gradient of the electron density should also be taken into account. This results in the so-called GGA functional family. Compared to the LDA, the exchange energy of GGA is

\[ E_x^{\text{GGA}}(n) = \int d^3r n \epsilon_x^{\text{LDA}}(n) F_x^{\text{GGA}}(s), \]  

(3.6)

where the enhancement factor \( F_x^{\text{GGA}} \) has the asymptotic behavior

\[ F_x^{\text{GGA}}(s) = 1 + \mu s^2 + \cdots (s \to 0), \]  

(3.7)

where \( s \) is the reduced density gradient

\[ s = \frac{|\nabla n|}{2k_F n}, \]  

(3.8)

\( k_F = (3\pi^2 n)^{1/3} \) is the Fermi wave vector and \( \mu \) is the parameter of gradient expansion.
The GGA correlation term is

\[ E_{c}^{\text{GGA}}(n) = \int d^3r n(r) \{ \epsilon_{c}^{\text{LDA}}(n) + \beta t^2(r) + \cdots \}, \quad (3.9) \]

\( \beta \) is a coefficient and \( t \) is

\[ t = \left| \frac{\nabla n}{2k_{TF} n} \right|, \quad (3.10) \]

\( k_{TF} \) is the appropriate reduced density gradient for correlation (fixed by Thomas-Fermi screening wave vector \( k_{TF} = (4k_F/\pi)^{1/2} \)).

For the spin polarized system, the PBE is written as

\[ E_{xc}^{\text{GGA}}(n^{\uparrow}, n^{\downarrow}) = \int d^3r n^{\uparrow} \epsilon_{xc}^{s}(n^s) F_{xc}(r_s, \zeta, s), \quad (3.11) \]

where

\[ \zeta = \frac{n^{\uparrow} - n^{\downarrow}}{n^{\uparrow} + n^{\downarrow}}. \quad (3.12) \]

The PBE functional is nowadays the most commonly used functional for solid-state calculations. There are no empirical parameters in PBE. The PBEsol has the same analytical form as the PBE. The differences between PBE and PBEsol are the values of \( \mu \) and \( \beta \).

### 3.1.2 Ultrasoft Pseudopotentials (USP) plane-wave method

The Bloch’s theorem shows that the electronic wavefunctions at each k-point can be expanded in terms of a discrete plane-wave basis set. The number of plane waves in this expansion should be infinite in principle. In practise the plane wave basis set can be truncated to include only plane waves that have kinetic energies that are smaller than some particular cutoff energy. The truncation of the basis set produces an error in the calculations of total energy. Increasing the value of the cutoff energy may reduce the magnitude of the error. According to the requirement of converge with respect to the number of plane waves, we need to choose the proper cutoff energy.

In the USP plane-wave total energy method, the accuracy of the pseudopotential is of particular importance. Vanderbilt introduced ultrasoft pseudopotentials (USP) in 1990 [21]. USPs are optimized to the plane-wave solid-state calculations and needs the lowest possible cutoff energy for the plane-wave basis set.

The general form of the pseudopotential is expressed as

\[ V_{NL} = \sum_{lm} |lm\rangle V_{i} \langle lm|, \quad (3.13) \]
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where \( V_l \) is the pseudopotential for angular momentum \( l \), \( |lm\rangle \) are the spherical harmonics.

In the USP plane-wave method, the nonlocal potential \( V_{NL} \) is given as

\[
V_{NL} = \sum_{n,m,I} D_{nm}^{(0)}|\beta_n^I\rangle\langle\beta_m^I|, \tag{3.14}
\]

where the projectors \( \beta \) and coefficients \( D^{(0)} \) characterize the pseudopotential and differ for different atomic species. For the derivations of \( \beta \) and \( D^{(0)} \), one can refer to Ref. [21, 22]. The index \( I \) refers to an atomic site. The valence charge density is defined as

\[
n(r) = \sum_i |\phi_i(r)|^2 + \sum_{nmI} Q_{nmI}(r)\langle \phi_i|\beta_n^I\rangle\langle\beta_m^I|\phi_i\rangle, \tag{3.15}
\]

where \( \phi \) are the pseudo-wave functions and \( Q(r) \) are the augmentation functions that are strictly localized in the core regions, viz.

\[
Q_{nm}(r) = \psi_n^*(r)\psi_m(r) - \phi_n^*(r)\phi_m(r), \tag{3.16}
\]

where \( \psi(r) \) are all-electronic wave functions. The \( \phi \) are constructed from \( \psi(r) \) and satisfy

\[
\langle \phi_i|S|\phi_j\rangle = \delta_{ij}, \tag{3.17}
\]

where \( S \) is a Hermitian overlap operator,

\[
S = 1 + \sum_{nmI} q_{nm}|\beta_n^I\rangle\langle\beta_m^I|, \tag{3.18}
\]

where coefficients \( q \) are obtained by integrating \( Q(r) \).

Kohn-Sham equation can be rewritten for the USP method as

\[
H|\phi_i\rangle = \epsilon_i S|\phi_i\rangle, \tag{3.19}
\]

where \( H \) can be presented as a sum of kinetic energy and local potential

\[
H = T_s + V_{eff}(r) + \sum_{nmI} D_{nmI}^I|\beta_n^I\rangle\langle\beta_m^I|, \tag{3.20}
\]

where \( V_{eff}(r) \) contains electron-nucleus \( V_{loc}^{\text{ion}}(r) \), Hartree potential and exchange-correlation terms. All the terms arising from the augmented part of electron density are grouped with the nonlocal part of the pseudopotential by defining new coefficients

\[
D_{nmI}^I = D_{nm}^{(0)} + \int dr V_{eff}Q_{nmI}(r). \tag{3.21}
\]
CHAPTER 3. *AB INITIO THEORY*

In the USP method, the eigenvalues from the pseudo potentials are equal to that from all-electron potentials. Their corresponding orbitals match exactly outside the core radii. Because the scattering properties are correct at each reference energy, the transferability can be systematically improved by increasing the number of such energies. The valence charge density is precisely equal to the all-electron valence density in the reference configuration [23].

### 3.1.3 Exact Muffin-tin Orbital (EMTO) method

The all electron muffin-tin method is appropriate method to solve $V_{\text{eff}}(r)$. Within the muffin-tin approximation, the effective potential is represented by non-overlapping spherically symmetric potentials around the atomic nuclei and a constant potential in the interstitial region. The exact muffin-tin orbital (EMTO) is the 3rd generation method in the muffin-tin approximation family. The EMTO method uses large overlapping muffin-tin potential spheres which can describe the exact one-electron potential rather accurately.

$$V_{\text{eff}} \approx v_{\text{mt}}(r) \equiv v_0 + \sum_R |v_R(r - R) - v_0|,$$

where $v_0$ is a constant potential, $v_R(r - R) - v_0$ are the spherical potential wells centered on lattice sites $R$. We can solve the Kohn-Sham equation (Eq. 3.3) by assuming a linear combination of the exact muffin-tin orbitals $\psi_{\text{RL}}^a(\epsilon_j, r_R)$ as following

$$\Psi_j(r) = \sum_{RL} \psi_{RL}^a(\epsilon_j, r_R) \psi_{RL,j}^a.$$

The expansion coefficients, $\psi_{RL,j}^a$ are determined in a way that $\Psi_j(r)$ is a solution for Eq. 3.3 in the entire space.

The exact muffin-tin orbitals are constructed using different basis functions inside the potential sphere ($r - R < s_R$) and in the interstitial region ($r - R > s_R$), herein $s_R$ is the radius of the potential sphere centered at site $R$. The basis functions used are called partial waves ($\Phi_{RL}^a$) inside the sphere and screened spherical waves ($\Phi_{RL}^a(\epsilon - V_0, r - R)$) in the interstitial zone.

Inside the potential sphere, the basis functions $\Phi_{RL}^a$, so called partial waves, are constructed from solutions of the scalar-relativistic, radial Dirac equations ($\Phi_{RL}$) and the real harmonics ($Y_L(r - R)$)

$$\Phi_{RL}^a(\epsilon, r - R) = N_{RL}^a(\epsilon) \Phi_{RL}(\epsilon, r - R) Y_L(r - R).$$

The normalization factor $N_{RL}^a(\epsilon)$ assures a proper matching at the potential sphere boundary to the basis function outside of the potential sphere.
In the interstitial region the screened spherical waves are solutions of the free electron Schrödinger equation. The boundary conditions for the free electron Schrödinger equation are given in conjunction with non-overlapping spheres, called hard spheres, centered at lattice site \( R \) with radius \( a_R \). The screened spherical waves are just defined as being free electron solutions which behave as real harmonics on their own \( a \)-spheres centered at site \( R \) and vanish on all the other sites.

These basis functions, partial waves and screened spherical waves, must join continuously and differentiable at \( a_R \). This is implemented using additional free electron wave functions \( \psi_{RL}(\epsilon, a_R) \), by which the connection between the screened spherical waves and the partial waves is obtained. It joins continuously and differentiable to the partial wave at \( s_R \) and continuously to the screened spherical wave at \( a_R \). Because of \( a_R < s_R \), the additional free-electron wave function should be removed, which is realized by the so-called kink-cancelation equation.

In the calculation of total energy, the EMTO method employs the Full Charge Density (FCD) technique, which not only improves the calculation efficiency but also ensures total energies with an accuracy similar to that of the full-potential methods. The total charge density is obtained by summations of one-center densities, which may be expanded in terms of real harmonics around each lattice site

\[
n(r) = \sum_R n_R(r - R) = \sum_{RL} n_{RL}(r - R)Y_L(r - R).
\]  

(3.25)

The total energy of the system is obtained via full charge density (FCD) technique using the total charge density. The space integrals over the Wigner-Seitz cells in Eq. 3.1 is solved via the shape function technique. The FCD total energy is expressed as

\[
E_{\text{tot}} = T_s[n] + \sum_R (F_{\text{intra}R}[n_R] + E_{\text{xc}R}[n_R]) + F_{\text{inter}}[n],
\]  

(3.26)

where \( T_s[n] \) is the kinetic energy, \( F_{\text{intra}R} \) is the electrostatic energy due to the charges inside the Wigner-Seitz cell, \( E_{\text{xc}R} \) is the exchange-correlation energy, and \( F_{\text{inter}} \) is the electrostatic interaction between the cells (Madelung energy).

**Coherent potential approximation (CPA)**

The Coherent Potential Approximation (CPA) was introduced by Soven for the electronic structure problem and by Taylor for phonons in random alloys [24, 25]. Later, Gyorffy formulated the CPA in the framework of the multiple scattering theory using the Green function technique [26]. In this theory, the real atomic potential is replaced by an effective (coherent) potential constructed from real atomic potentials of the alloy components. The impurity atoms/alloy components are then embedded into this effective potential. Two main approximations are applied. First, it is assumed that the local
potentials around a certain type of atom from the alloy are the same, i.e. the effect of local environments is neglected. Second, the system is replaced by a monoatomic set-up described by the site independent coherent potential $\tilde{P}$.

**EMTO-CPA**

Today, CPA represents the most efficient alloy theory for the electronic structure calculations in multicomponent random solid solutions. The CPA has been successfully implemented in the EMTO method [27]. The single-site nature of the CPA limits its applicability to systems with negligible short-range order and local lattice relaxation effects. Nevertheless, it turned out that the EMTO-CPA method can accurately capture the structural energy differences and trace energy changes related to lattice distortions in complex alloys.

The contents of the EMTO-CPA above are from Ref. [28].
Chapter 4

Interlayer potentials

4.1 Fitting the interlayer potentials

Based on *ab initio* calculations, we used the Chen-Möbius inversion to get the ILPs. In order to be able to provide the ILPs for an arbitrary distance, we need to assume an analytical expression and fit the *ab initio* data using that form. According to the distributions of the data, we employ different fitting functions.

4.1.1 Interlayer potentials for metals

For fitting the converted interlayer potentials inverted from the CASTEP calculations, we used the Rahaman-Stillinger-Lemberg (RSL2) function

\[ \phi_{ij} = D_0 e^{y\left(1 - \frac{r_{ij}}{R_0}\right)} + \frac{a_1}{1 + e^{b_1(r_{ij} - c_1)}} + \frac{a_2}{1 + e^{b_2(r_{ij} - c_2)}} + \frac{a_3}{1 + e^{b_3(r_{ij} - c_3)}}. \]  

(4.1)

Here \( r_{ij} \) represents the interlayer distance. Note that there are totally 12 adjustable parameters in this function \((D_0, y, R_0, a_1, a_2, a_3, b_1, b_2, b_3, c_1, c_2, \text{ and } c_3)\) and thus it offers a rather flexible form to describe the pair interactions between layers. In Table 4.1, we list the parameters. \( R_0 \) is often set to 1.0.

The ILP \( \phi_{ab} \) is similar to the interatomic pair potential. At the equilibrium interlayer distance, the ILP \( \phi_{ab} \) takes its minimum value. Note that ILP \( \phi_{aa} \) is plotted only for large interlayer distances, since Eqs. 2.4 and 2.5 involve \( \phi_{aa}(d) \) only for \( d \geq 2d \).
CHAPTER 4. INTERLAYER POTENTIALS

Figure 4.1. The CASTEP ILPs $\phi_{ab}$ (a) and $\phi_{aa}$ (b) of fcc (111) planes for Al, the discrete points are the *ab initio* data obtained by Chen-Möbius inversion and the lines represent the fitting potentials.

Table 4.1. The RSL2 parameters of the ILPs $\phi_{ab}$ and $\phi_{aa}$ from Eq. (4.1). The units are indicated.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\phi_{ab}$</th>
<th>$\phi_{aa}$</th>
<th>Parameter</th>
<th>$\phi_{ab}$</th>
<th>$\phi_{aa}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ (eV)</td>
<td>-7.372035</td>
<td>-302.853273</td>
<td>$a_2$ (eV)</td>
<td>-602.0528</td>
<td>-69.426275</td>
</tr>
<tr>
<td>$R_0$ (Å)</td>
<td>1.000000</td>
<td>1.000000</td>
<td>$b_2$ (Å$^{-1}$)</td>
<td>2.819443</td>
<td>7.853272</td>
</tr>
<tr>
<td>$y$</td>
<td>1.412776</td>
<td>2.588845</td>
<td>$c_2$ (Å)</td>
<td>1.766391</td>
<td>0.000432</td>
</tr>
<tr>
<td>$a_1$ (eV)</td>
<td>8381.2168</td>
<td>-0.243731</td>
<td>$a_3$ (eV)</td>
<td>-7620.8720</td>
<td>0.651101</td>
</tr>
<tr>
<td>$b_1$ (Å$^{-1}$)</td>
<td>3.150760</td>
<td>365.406083</td>
<td>$b_3$ (Å$^{-1}$)</td>
<td>3.23390</td>
<td>9.464628</td>
</tr>
<tr>
<td>$c_1$ (Å)</td>
<td>1.567630</td>
<td>3.698911</td>
<td>$c_3$ (Å)</td>
<td>1.565706</td>
<td>1.409775</td>
</tr>
</tbody>
</table>
4.1. FITTING THE INTERLAYER POTENTIALS

4.1.2 Interlayer potentials for alloys

In the calculations of Pd, Ag and Pd-Ag alloy with the EMTO-CPA method, we used
the Morse function [29] to fit the discrete data. We found that the Morse function could
represent well the data of the inversion of ILPs. The Morse function is an exponential
function

\[ E(w) = a + be^{-\lambda d} + ce^{-2\lambda d} \]

written in terms of the average interlayer distance \( d \). Here \( \lambda, a, b \) and \( c \) are the four
independent Morse parameter. In order to clearly express the ILP \( \phi_{ab} \), we can write the
Morse function in another form:

\[ \phi_{ab}(d) = D_0 e^{-\gamma \left(\frac{d}{R_0} - 1\right)} - 2D_0 e^{-\gamma \left(\frac{d}{R_0} - 1\right)} + E_0. \]

Another exponential function is used to fit the \( \phi_{aa} \)

\[ \phi_{aa}(d) = Y_0 + A_1 e^{-\frac{d}{T_1}} + A_2 e^{-\frac{d}{T_2}}. \]

The parameters \( D_0, \gamma, R_0, E_0, Y_0, A_1, A_2, T_1 \) and \( T_2 \) were obtained by numerical fitting.
Figure 4.2 shows the interlayer potential \( \phi_{ab} \) and \( \phi_{aa} \) for the fcc (111) planes of Pd.
4.2 Assessing the interlayer potentials

By contrasting the energies of the ABC and AB models as derived from the ILPs and the original *ab initio* total energies, we learn about the accuracy of the inversion and fitting procedures. Figure 4.3 shows this comparison taken Al as example. We find that the ILPs reproduce well the results of the *ab initio* calculations from CASTEP method.

For the IILPs derived from the EMTO-CPA method, we compared the energies of the ABC and AB model derived from the interlayer potentials (i.e. Eqs. 2.4 and 2.5) with the *ab initio* total energies, At the same time, we also employed the ABAC model to check the ILPs (in Eq. 2.6). A comparison is shown for Ag in Figure 4.4 for the ABC model (upper panel), AB model (middle panel) and ABAC model (lower panel). We find that the present interlayer potentials reproduce well the results of the *ab initio* calculations including the ABAC model system which was not used to derive the potential.

The good agreement between the ILPs and *ab initio* calculations demonstrates the robustness of our approach.

**Figure 4.3.** Comparison between the *ab initio* total energies of the structure model ABC (panel a) and AB (panel b) (symbols) and the corresponding total energies obtained from the ILPs (lines). The energies are plotted as a function of interlayer separation.
4.2. ASSESSING THE INTERLAYER POTENTIALS

Figure 4.4. Comparison between the *ab initio* total energy and the one calculated with the ILPs for the Ag. Results are shown for the ABC model (upper panel), AB model (middle panel) and ABAC model (lower panel).
Chapter 5

Properties related to atomic layers

5.1 Elastic constant $C_{44}$

For cubic crystals, there are three independent single-crystal elastic constants $C_{11}$, $C_{12}$ and $C_{44}$. The elastic constant $C_{44}$ is often referred to as the shear elastic constant and is based on the deformation of the crystal along the fcc $\langle 111 \rangle$ direction. It is defined as the second order derivative of the total energy with respect to the lattice strain. Using the present ILPs, $C_{44}$ may be expressed in terms of the second order derivatives of the $\phi_{ab}(d)$ and $\phi_{aa}(d)$ potentials as a function of the interlayer separation $d$.

We notice that changing the interlayer distance while keeping the in-plane lattice constants fixed leads to volume change. This gives a term proportional to the bulk modulus, which should be taken into account when extracting $C_{44}$ from the above total energy curvature.

5.2 Stacking fault energy

In close-packed lattices, the partial dislocations are connected by stacking faults. The size of the stacking fault energy ($\gamma_{sf}$) determines the width of the faulted ribbon and by that influences the dislocation propagation mechanism and ultimately the plastic deformation. In fcc metals, one can distinguish intrinsic stacking fault (ISF), extrinsic stacking fault (ESF) and twin stacking fault (TSF).

The ideal fcc $(111)$ arrangement is shown in Figure 5.1a. In this system the stacking is $\cdots$ABC ABC ABC ABC $\cdots$ (Figure 5.1b), i.e. a periodically repeated ABC sequence. Introducing a stacking mistake leads to the so called stacking fault. The intrinsic fault is displayed in Figure 5.1c. This is obtained by removing one atomic layer from the ideal fcc $(111)$ arrangement and can be expressed as $\cdots$ABC ABC ABC $\upharpoonright$ BC ABC ABC $\cdots$
5.2. STACKING FAULT ENERGY

Figure 5.1. The stacking arrangement for fcc (111) planes, the perfect stacking arrangement (a), one dimension arrangement of viewing each layer as a unity (b) and (d), the stacking arrangement with an intrinsic fault (c).

(Figure 5.1d), where : marks the “missing” layer.

The formation energy per area of a stacking fault in an otherwise perfect crystal is determined by the energy difference between structures with \( E_{sf} \) and without \( E_t \) the stacking fault, viz.

\[
\gamma_{sf} = \frac{E_{sf} - E_t}{A},
\]

where \( E_t \) refers to the same number of layers (N) as the faulted structure and A is the area of the stacking fault plane.

In \textit{ab initio} calculations of the stacking fault energy, the supercell approach and the axial interaction model (AIM) have been applied [30, 31]. A comparison of these two approaches has been reported [32]. In the supercell model, \( E_{sf} \) represents the total energy of a supercell containing \( N \) layers and one stacking fault and \( E_t = NE_{fcc} \), where \( E_{fcc} \) is the energy per atom of the ideal fcc stacking. Within the AIM approach including interactions up to the third order, the ISF energy may be expressed as

\[
\gamma_{sf} = \frac{E_{hcp} + 2E_{dhcp} - 3E_{fcc}}{A}.
\]

In this expression all total energies are per atom. The total energies from Eqs. 5.1 and 5.2 can be determined either by direct DFT calculations or via Eqs. 2.4, 2.5 and 2.6 using
the ILPs.

For intrinsic stacking faults, the stacking fault energy is expressed directly with ILPs as following

$$\gamma_{sf} = \sum_{n=1}^{\infty} (3n-1)\left[ \phi_{aa}((3n-1)d) - \phi_{ab}((3n-1)d) \right] + (3n)\left[ \phi_{ab}(3nd) - \phi_{aa}(3nd) \right]$$  \hspace{1cm} (5.3)

The extrinsic stacking fault (ESF) is obtained by inserting an extra layer in the ideal fcc (111) arrangement. Its stacking is \ldots ABC ABC \ldots B \ldots ABC ABC \ldots, which is also viewed as two next-nearest intrinsic stacking faults. While the twin stacking fault is a plane boundary between two fcc stacking sequences with opposite orientation, i.e. \ldots ABCABACBA\ldots.

5.3 Surface energy

The surface energy is defined as the surface excess free energy per unit area of a particular crystal facet. The surface energy is often calculated using the supercell model in Figure 5.2. We construct a supercell consisting of \(N\) atomic layers perpendicular to the surface and separated by a wide vacuum layer that prevents the interaction between neighboring surfaces. Then the surface energy is given by the formula

$$\gamma_s = \frac{E_s - NE_{\text{fcc}}}{2A},$$  \hspace{1cm} (5.4)

where \(E_s\) is the total energy of the supercell, \(E_{\text{fcc}}\) is the bulk energy per layer and the factor 2 arises from the two surfaces of the slab. The above energies can be computed either by direct \textit{ab initio} calculations or using the ILPs.

Alternatively, in the case of the ILP-based description of the fcc (111) surface, we may consider a semi-infinite surface geometry \ldots CBACBAVacuum\ldots, so that there is only one surface layer. Then the surface energy is the sum of the ILPs between the atomic layers and the removed layers, \textit{viz.}

$$\gamma_s = -\sum_{k=1}^{\infty} \left[ (3k-2)\phi_{ab}((3k-2)d) + (3k-1)\phi_{ab}((3k-1)d) + 3k\phi_{aa}(3kd) \right],$$  \hspace{1cm} (5.5)

where \(k\) represents a layer in the surface model and also indicates the number of interaction under a certain interlayer distance.
5.4 PHONON DISPERSION

Figure 5.2. Schematic plot of the structures used to calculate the surface energy. Panel (a): perfect fcc (111) stacking arrangement; panel (b): 12-atomic layers slab geometry separated by vacuum.

5.4 Phonon dispersion

The vibration of atoms in the crystal is correlated and the collective vibration forms a wave of allowed wavelength and amplitude. The quantum of such lattice vibration is called phonon. The phonon dispersion describes the wave vector dependence of the phonon frequencies.

To establish the phonon spectra for a system, we first get the force constant matrix, given by the second order derivative of the internal energy with respect to the Cartesian coordinates. The force constant matrix, \( F \), between two atoms \( i \) and \( j \) is given by

\[
F_{ij}(k) = \sum_R \left( \frac{\partial^2 U}{\partial \alpha \partial \beta} \right) e^{ik(r_{ij}+R)},
\]

(5.6)

where \( \alpha \) and \( \beta \) are position vectors in the Cartesian coordinates. The dynamical matrix \( D \) is

\[
D_{ij} = \frac{1}{(m_i m_j)^{1/2}} F_{ij}(k),
\]

(5.7)

where \( m_i \) and \( m_j \) are the masses of atom \( i \) and \( j \). Further details about the phonon dispersion from the force constant matrix are discussed as in Ref. [33].
Chapter 6

Results for metals and Pd-Ag alloys

6.1 Equilibrium properties

In order to get ILPs, we need to calculate equilibrium lattice parameter and cohesive energy. Choosing the proper exchange-correlation approximation functional is particularly important. Different exchange-correction functionals have been compared in Refs. [34, 35, 36, 37, 38]. It was reported that PBE often overestimates the lattice constants and underestimates the cohesive energy. On the other hand, PBEsol may accurately describe the equilibrium properties of dense solids and their surfaces [39]. In the present thesis, we employed the PBE generalized gradient approximation for Al, Ni, Cu, Ag and Au in CASTEP and the modified PBE (PBEsol) for Pd-Ag random alloy in EMTO.

Table 6.1. Theoretical lattice constants (\(a\), in units of Å), nearest interatomic distances within the fcc (111) layers (\(a_{0}\), in units of Å), the interlayer distances (\(d_{0}\), in units of Å) for five fcc metals. For comparison, some experimental lattice constants and the deviations between theory and experiment (\(\Delta a/a\), in %) are also shown.

<table>
<thead>
<tr>
<th>Metal (PBE)</th>
<th>Al</th>
<th>Ni</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>4.0492</td>
<td>3.5294</td>
<td>3.6261</td>
<td>4.1384</td>
<td>4.1811</td>
</tr>
<tr>
<td>(d_{0})</td>
<td>2.8634</td>
<td>2.4918</td>
<td>2.5560</td>
<td>2.8890</td>
<td>2.8838</td>
</tr>
<tr>
<td>(\Delta a/a)</td>
<td>0.01</td>
<td>0.15</td>
<td>0.32</td>
<td>1.29</td>
<td>2.51</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal (Exp.)</th>
<th>Al</th>
<th>Ni</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{0})</td>
<td>2.3381</td>
<td>2.0346</td>
<td>2.0871</td>
<td>2.3589</td>
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<td>(\Delta a/a)</td>
<td>0.01</td>
<td>0.15</td>
<td>0.32</td>
<td>1.29</td>
<td>2.51</td>
</tr>
</tbody>
</table>
6.1. EQUILIBRIUM PROPERTIES

6.1.1 Al, Ni, Cu, Ag and Au

For the elemental Al, Ni, Cu, Ag and Au metals, Table 6.1 shows the calculated lattice parameters ($a$), the distance between two nearest neighboring atoms inside the close packed atomic layers ($a_0$), and the equilibrium interlayer distance ($d_0$) for the ABC structure model. In general, the theoretical and experimental data are consistent with each other, the average relative deviation between theory and experiment being below 1%. The lattice parameters of Al, Ni and Cu are in good agreement with the experimental data, whereas the PBE lattice parameters are somewhat larger than the corresponding experimental values for Ag and Au.

6.1.2 Pd, Ag and Pd-Ag random alloys

Considering the large difference between the calculation from the PBE results and the experimental data, we decided to use the PBEsol approximation to calculate the Ag, Pd and Pd-Ag alloys in the EMTO-CPA method. Our calculations shown in Table 6.2 are in good agreement with the experimental data.

Since EMTO is a muffin-tin method, special care must be taken on how the energies are computed with this method for large interlayer distances. To this end, first we construct two hexagonal structures with six layers as the ABCABC and ABABAB models. By that we can minimize the errors coming from different Brillouin zone samplings. Next, when changing $d$ we ensure that the linear overlap between the individual atomic spheres (muffin-tin potential wells) remains below 15% in order to keep the overlap error small [28, 40]. Within this constrain, the range of “allowed” $d/a_0$ values ($a_0$ is the equilibrium interatomic distance in the fcc lattice) in EMTO calculations is set to 0.717-0.919. To illustrate the degree of lattice distortion upon changing $d/a_0$, in Figure 6.1 we show the Madelung constants of the ABC and AB structures as a function of $d/a_0$. It is seen that within the above $d/a_0$ interval, the ideal fcc or hcp Madelung constants (both of them being close to $\sim 1.7917$) drop below 1.7870, indicating a substantial reduction of the packing ratio as the interlayer distance starts to deviate from its equilibrium value by more than $\pm 0.1a_0$. For such open structures, the accuracy of the muffin-tin approximation is not sufficient to produce highly accurate energies and thus interlayer potentials. In order to overcome this problem, in EMTO calculations we consider additional systems with interlayer separation equal with the double of the equilibrium separation $d_{ABC}$ or $d_{AB}$. Namely, for the ABC (AB) model we set up a supercell with unit cell containing six (four) layers ordered according to AcBaCb (AcBc), where the capital letter stand for atoms and small letters for empty sites, containing empty potential wells. With so the dressed-up structure we are able to compute $E_{ABC}(2d_{ABC})$ and $E_{AB}(2d_{AB})$ with sufficiently high accuracy (see the separate symbols around 4.7 Å, in Figure 4.4).
Figure 6.1. The Madelung constant versus $d/a_0$ value for the ABC and AB structural models.

Table 6.2. Equilibrium lattice constants ($a$) for fcc Pd, Ag and Pd$_{0.5}$Ag$_{0.5}$. The experimental results corrected for the zero-point phonon term are shown in parentheses [48, 49]. The quoted experimental values for Pd$_{0.5}$Ag$_{0.5}$ were obtained for Pd$_{0.5087}$Ag$_{0.4913}$ (3.9766 Å) and Pd$_{0.462}$Ag$_{0.538}$ (3.9850 Å) [50]. Previous theoretical values were obtained using full-potential methods [46, 47] as well as the EMTO-CPA method [51]. In the lower panel of the table, $a_0$ and $d_0$ stand for the equilibrium nearest-neighbor distance in the fcc (111) plane and the equilibrium interlayer distance perpendicular to the (111) plane as determined from the corresponding calculated $a$ values. $d_{ABC}$ and $d_{AB}$ are the calculated equilibrium interlayer distance for fcc (111) and hcp (0001) models, respectively. All parameters are expressed in units of Å.

<table>
<thead>
<tr>
<th></th>
<th>Pd(EMTO)</th>
<th>Pd(CASTEP)</th>
<th>PdAg(EMTO)</th>
<th>Ag(EMTO)</th>
<th>Ag(CASTEP)</th>
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</thead>
<tbody>
<tr>
<td>$a$ (DFT)</td>
<td>3.8908</td>
<td>3.8795</td>
<td>3.9721</td>
<td>4.0681</td>
<td>4.0605</td>
</tr>
<tr>
<td>$a$ (Expt.)</td>
<td>3.881 (3.877) [48]</td>
<td>3.9766 [50]</td>
<td>4.069 (4.064) [48]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (Theo.)</td>
<td>3.879 (3.875) [49]</td>
<td>3.9850 [50]</td>
<td>4.061 (4.056) [49]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$ (Error)</td>
<td>+0.4%</td>
<td>-0.06%</td>
<td>-(0.11~0.32)%</td>
<td>+0.1%</td>
<td>-0.08%</td>
</tr>
<tr>
<td>$a_0$</td>
<td>2.7512</td>
<td>2.7432</td>
<td>2.8087</td>
<td>2.8766</td>
<td>2.8712</td>
</tr>
<tr>
<td>$d_0$</td>
<td>2.2646</td>
<td>2.2389</td>
<td>2.2933</td>
<td>2.3487</td>
<td>2.3443</td>
</tr>
<tr>
<td>$d_{ABC}$</td>
<td>2.2460</td>
<td>2.2419</td>
<td>2.2933</td>
<td>2.3489</td>
<td>2.3343</td>
</tr>
<tr>
<td>$d_{AB}$</td>
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<td>2.2659</td>
<td>2.3080</td>
<td>2.3603</td>
<td>2.3389</td>
</tr>
</tbody>
</table>
6.2 Cubic shear elastic constant $C_{44}$

Taking Pd, Ag and Pd-Ag alloys as examples, we compared the $C_{44}$ from the ILPs with experimental data and \textit{ab initio} calculations. The data from the ILPs are in good agreement with the \textit{ab initio} calculations. The results of the EMTO method are consistent with those from the CASTEP calculations. All theoretical results are slightly larger than the experimental data.

<table>
<thead>
<tr>
<th></th>
<th>Pd(EMTO)</th>
<th>Pd(CASTEP)</th>
<th>PdAg(EMTO)</th>
<th>Ag(EMTO)</th>
<th>Ag(CASTEP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{44}$ (ILP)</td>
<td>105</td>
<td>107</td>
<td>83</td>
<td>55</td>
<td>61</td>
</tr>
<tr>
<td>$C_{44}$ (DFT)</td>
<td>112 [51]</td>
<td>92$^a$</td>
<td>94 [51]</td>
<td>61 [51]</td>
<td>69$^a$</td>
</tr>
<tr>
<td>$C_{44}$ (Expt.)</td>
<td>71.2 [52]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>51.1 [52]</td>
</tr>
</tbody>
</table>

$^a$ results obtained for the ideal interlayer distance.

6.3 Stacking fault energy

The values of stacking fault energy are usually very small (order of 10-200 mJ/m$^2$). Thus obtaining accurate stacking fault energy is a rather difficult task in the experiments. Due to the experimental uncertainties involved (e.g., temperature and alloying effects), the reported values show large scatter listed in Table 6.4. In our calculations of the stacking fault energy for Al, Ni, Cu, Ag and Au, we constructed the supercell with 12 layers and 14 Å vacuum layers for the perfect stacking and the stacking with intrinsic stacking fault. In the supercell method, the intrinsic stacking fault is the middle of 12 layers, the same surface layers are constructed for the two stackings. So the total energy difference between two stackings is the intrinsic fault energy. We found a good agreement between the stacking fault energies from the ILPs and \textit{ab initio} calculations (Table 6.4).

For Pd-Ag alloys and Pd and Ag, in addition to the comparisons between the supercell and AIM results, we also contrast the values from EMTO and CASTEP.

The ILPs may be used to establish the interaction between two intrinsic stacking faults located within the same plane family. To this end, we considered an ideal fcc supercell $\cdots$ABCABCABCABC$\cdots$ from which we removed two layers separated by a specific number of atomic layers ($N_s$). For instance, in $\cdots$ABC:BCA:CABC$\cdots$ (where $:$ stands for the missing layer) the two ISFs are separated by three atomic layers ($N_s = 3$). The EMTO-ILP formation energies for the above double-ISF in Pd, Ag and Pd$_{0.5}$Ag$_{0.5}$ are plotted in Figure 6.2 as a function of the number of layers separating the two faults. It
is expected that with increasing $N_s$, the energy of double-ISF should converge to twice of that of the ISF from Table 6.3 (ILP supercell results). Indeed, for all three systems the double-ISF energy reaches with good accuracy the converged value already for $N_s \geq 3$. For smaller separations, there is a clear attractive interaction between the ISFs. To understand this, we should realize that when the two ISFs become next-nearest neighbors ($N_s = 1$), then the double-ISF reduces to an extrinsic stacking fault, \( \text{viz.} \) configuration · · ·ABC:B:ABCABC···. The calculated (EMTO-ILP) ESF energies are 192.4, 20.6 and 89.6 mJ/m$^2$ for Pd, Ag and Pd$_{0.5}$Ag$_{0.5}$, respectively. These values are marginally larger than the corresponding ISF energies, meaning that energetically it is slightly more favorable to have one ESF than two ISFs. It is noticeable that the double-ISF→ESF reconstruction happens without a sizable energy barrier (except the one associated with the shift of the atomic layers parallel to the stacking fault).

Using the ILPs derived from EMTO calculations, we also determined the formation energy of a twin stacking fault described by the configuration · · ·ABCBCBACBA··· for Pd, Ag and Pd$_{0.5}$Ag$_{0.5}$. The theoretical TSF energies are 155.7, 9.9 and 52.0 mJ/m$^2$, respectively. The small values of TSF indicate that these faults are created much easier than the intrinsic and the extrinsic stacking faults.
### Table 6.4. Stacking fault energies \((\gamma_{sf}, \text{in units of mJ/m}^2)\) for Al, Ni, Cu, Ag, and Au. The displayed data are as follows: ILP present results obtained using the interlayer potentials; DFT present results obtained from direct DFT calculations; TBP, TB: calculations based on tight-binding method; FLMTO: results of full potential linear-muffin-tin orbitals calculations; EAM: calculations from the embedded-atom-method potentials.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Al</th>
<th>Ni</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILP</td>
<td>180</td>
<td>213</td>
<td>33</td>
<td>16</td>
<td>26</td>
</tr>
<tr>
<td>DFT</td>
<td>180</td>
<td>183</td>
<td>34</td>
<td>22</td>
<td>41</td>
</tr>
<tr>
<td>TBP [53]</td>
<td>–</td>
<td>305/265</td>
<td>21/15</td>
<td>1/0</td>
<td>–</td>
</tr>
<tr>
<td>TB [54]</td>
<td>96</td>
<td>–</td>
<td>18</td>
<td>29</td>
<td>50</td>
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<tr>
<td>FLMTO [55, 56]</td>
<td>164</td>
<td>–</td>
<td>46</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Potential [57]</td>
<td>146.0/95.4</td>
<td>304.4/120.3</td>
<td>20.6/33.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>EAM [58]</td>
<td>352/361</td>
<td>104/109</td>
<td>119/121</td>
<td>67/73</td>
<td>41/44</td>
</tr>
<tr>
<td>EAM [59]</td>
<td>146.47</td>
<td>90.99</td>
<td>74.59</td>
<td>44.19</td>
<td>61.58</td>
</tr>
<tr>
<td>Exp. [60]</td>
<td>170/200/240</td>
<td>64-140/410</td>
<td>40/169</td>
<td>21/26-58</td>
<td>24-47</td>
</tr>
<tr>
<td>Exp. [61]</td>
<td>166</td>
<td>64-140/410</td>
<td>40/45/169</td>
<td>24-47</td>
<td>16/43/58</td>
</tr>
<tr>
<td>Exp. [62]</td>
<td>166</td>
<td>128/250</td>
<td>48/55/78</td>
<td>16/22</td>
<td>–</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pd(EMTO)</th>
<th>Pd(CASTEP)</th>
<th>PdAg(EMTO)</th>
<th>Ag(EMTO)</th>
<th>Ag(CASTEP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma_{sf}(\text{ILP})^a)</td>
<td>185.6</td>
<td>199.3</td>
<td>81.1</td>
<td>15.0</td>
</tr>
<tr>
<td>(\gamma_{sf}(\text{ILP})^b)</td>
<td>186.9</td>
<td>227.0</td>
<td>87.9</td>
<td>16.8</td>
</tr>
<tr>
<td>(\gamma_{sf}(\text{DFT})^a)</td>
<td>185.0</td>
<td>178.5(^c)</td>
<td>76.8</td>
<td>26.6</td>
</tr>
<tr>
<td>(\gamma_{sf}(\text{DFT})^b)</td>
<td>192 [63]</td>
<td>164.3(^c)</td>
<td>83 [63]</td>
<td>23 [63]</td>
</tr>
<tr>
<td>(\gamma_{sf}(\text{Expt.})^a)</td>
<td>180 [64]</td>
<td>–</td>
<td>79.9 [65]</td>
<td>22.8 [66]</td>
</tr>
</tbody>
</table>

\(^a\) AIM results; \(^b\) supercell results; \(^c\) results obtained for the ideal interlayer distance.
6.4 Surface energy and surface relaxation

The surface energies calculated with the ILPs and DFT are listed in Table 6.5. In general, the ILPs and DFT formation energies are consistent with each other. For Ag (Pd) both EMTO and CASTEP results based on the ILP calculations are slightly smaller (larger) than the those calculated directly (DFT). On the other hand, for Pd\textsubscript{0.5}Ag\textsubscript{0.5} alloy, the DFT and ILP values turn out to be very close to each other. Beyond the obvious numerical errors associated with surface energy calculations, one possible explanation for the above discrepancies is that the surface physics is not completely captured by the ILPs.

The surface energies of close-packed metal surfaces show a weak layer relaxation dependence. The ILPs may be used to establish the size of the surface relaxation and its impact on the formation energy. Changing the interlayer distance between surface layer and its nearest neighboring layer in the semi-infinite surface geometry, we calculated a series of surface energies and used the interpolation method to obtain the smallest surface energy $\gamma_{sr}$, whose corresponding surface interlayer distance is $d_{12}^s$ after surface relaxation (shown in Table 6.5). The present theoretical equilibrium surface (top-layer) and bulk interlayer distances are shown in Table 6.5. For all three metals, the fcc (111) surfaces show small outward relaxations characteristic to the close-packed surfaces of late transition metals [67, 68, 69, 70]. However, the impact of surface relaxation on the surface formation energy in all cases remains below 0.5\%, which is consistent with the negligible effect reported for 4d metals [71].

**Table 6.5.** Surface energy $\gamma_s$ (in mJ/m$^2$), bulk equilibrium interlayer distance $d_{12}^b$ (in Å), and surface equilibrium interlayer distance $d_{12}^s$ (in Å). For ILP, the numbers in parenthesis are the surface energies obtained for the semi-infinite surface model. $\gamma_{sr}$ (in mJ/m$^2$) represent the surface energy after surface relaxation.

<table>
<thead>
<tr>
<th></th>
<th>Pd(EMTO)</th>
<th>Pd(CASTEP)</th>
<th>PdAg(EMTO)</th>
<th>Ag(EMTO)</th>
<th>Ag(CASTEP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma_s$(ILP)</td>
<td>2377.4</td>
<td>2189.0</td>
<td>1584.4</td>
<td>891.1</td>
<td>959.9</td>
</tr>
<tr>
<td></td>
<td>(2378.4)</td>
<td>(2192.9)</td>
<td>(1584.7)</td>
<td>(891.1)</td>
<td>(959.9)</td>
</tr>
<tr>
<td>$\gamma_s$(DFT)</td>
<td>2076</td>
<td>1877</td>
<td>1591</td>
<td>1201</td>
<td>1047/1235$^a$</td>
</tr>
<tr>
<td>$d_{12}^b$</td>
<td>2.2460</td>
<td>2.2419</td>
<td>2.2933</td>
<td>2.3489</td>
<td>2.3343</td>
</tr>
<tr>
<td>$d_{12}^s$</td>
<td>2.2880</td>
<td>2.2764</td>
<td>2.3219</td>
<td>2.3674</td>
<td>2.3513</td>
</tr>
<tr>
<td>$\gamma_{sr}$(ILP)</td>
<td>2365.2</td>
<td>2185.7</td>
<td>1579.7</td>
<td>889.7</td>
<td>958.5</td>
</tr>
</tbody>
</table>

$^a$ 1047 mJ/m$^2$ for interlayer distance 2.3343 Å and 1235 mJ/m$^2$ for interlayer distance 2.3443 Å.
6.5 Phonon dispersion

Possessing the phonon spectrum, one can predict a series of thermo-physical properties. The phonon dispersions are represented by the interatomic forces derived from the interatomic potentials. Here we calculated the phonon dispersion for the fcc (111) planes using the ILPs. Viewing the whole fcc (111) layer as a unit, we consider the mass of the atoms in the $\sqrt{3}a^2/4$ area as the ‘mass’ of the layer ($a$ is the fcc lattice constant from Table 6.1). For each layer, we use the ‘equivalent-atom’ model to represent the total layer and the masses of these ‘equivalent-atoms’ are identical.

Although the three layers in the fcc (111) planes are only different because of the relative position of atoms, the one-dimension primitive cell contains three different atoms in our phonon calculations, so there are six branches in the phonon dispersion. Note that the optical branches from Figure 6.3 are in fact the folded-in acoustic branches (there is no gap at the zone boundary between the branches). In the fcc with one atom per primitive cell, the real phonon dispersion only has two acoustical branches along the fcc $\langle111\rangle$ direction, with degenerated transversal branches. Since we investigate the interactions along one direction, the distinct number of phonon branches is reduced along the principal symmetry direction G-Z as shown in Figure 6.3. Here we would like to make an Erratum to the Supplements: in the figure of the dispersion phonon from the published papers there is a small mistake in the transversal phonon branch as a result of the employed phonon-calculation software.
Furthermore, the phonon density of states from the Supplements represent the density of states of a hypothetical one-dimensional lattice and thus should not be compared to the real three-dimensional results.

The interlayer interaction for Pd is stronger than that for Ag, and thus the vibrational frequencies versus $k$ for Ag are weaker than those for Pd. The vibrational frequency of the Pd$_{0.5}$Ag$_{0.5}$ alloy is in between those obtained for Pd and Ag metals. To our knowledge, this is the first phonon spectra presented for completely random alloy and calculated using the mean-field coherent potential approximation.
Concluding remarks and Future work

Based on \textit{ab initio} calculations, we employed the Chen-Möbius inversion technique to derive the interlayer potentials (ILPs) in metals and alloys.

ILPs suit to describe the properties related to layers in layered materials. The errors of the ILPs mainly result from the errors of the \textit{ab initio} calculations and the numerical fitting procedure. Once the interlayer cohesive energy in some layered materials is accurately obtained, the interpolation method may be used to improve the accuracy of the fitting. We should mention that due to the complex magnetic interactions along the close-packed layers, there are some limitations for using the ILPs to investigate the related properties of magnetic materials. For the present systems, the high accuracy of the ILPs originates from the fact that the total layer is considered as a unit and in a layered materials the interlayer interactions are usually much weaker than the interaction within the layer. For some layered materials, for example graphite and BN, \textit{ab initio} tools do not accurately describe the interlayer cohesive energy. In such cases, one may use the Chen-Möbius inversion method to get accurately ILPs starting from the experimental data.

The present results obtained for random solid solutions shows that the EMTO-CPA method is a powerful tool to investigate complicated alloys and is able to provide accurate ILPs.

For future works, I will use the EMTO-CPA method to study the high entropy alloys (HEAs) which have already attracted a great attention in the field of metallurgy. The HEAs generally have at least 4 major equal-molar metallic elements. Experiments indicate that the HEAs have many interesting properties, such as a single solid solution phase (fcc, bcc or fcc and bcc), high strength, good wear, corrosion resistance, etc. It is particularly difficult to use conventional \textit{ab initio} atomistic simulation methods to investigate these systems. That is because HEAs are chemically and often also magnetic disordered multicomponent extended solid solutions. After performing an intensive theoretical investigation of the HEAs, we will use the above ILPs technique to describe the layer dependent properties of this complex and promising family of engineering alloys.
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Bibliography


