Chapter 5

Strain field due to interstitial H in Cu and Pd

5.1 Introduction

The presence of point defects in a crystal, such as vacancy or impurity atom, generally causes the displacement of the neighboring host atoms from their ideal lattice positions. Such lattice distortions are measured using X-ray diffraction and more recently by x-ray absorption fine structure (EXAFS) experiments. From theoretical point of view the problem of point defects especially the interstitial impurity in metallic system is difficult due to difficulties in calculating the short range interatomic potentials.

For the understanding of metal-hydrogen system, information about the microscopic interaction between the interstitial hydrogen and the surrounding host-metal atoms is essential. However, in spite of much information accumulated in the literature, there are still open questions regarding the forces and the displacements of the nearest neighbors (NN's) of the interstitial hydrogen atom, as most of the interatomic potentials fail at the distance where the interstitial atom occupies its position in the lattice. The recent study about the interaction potential of interstitial hydrogen with Pd using First Principle calculation, due to Elsasser [1] has improved the understanding of forces between the hydrogen and Pd atom and this motivates us to study the hydrogen-metal systems in detail using First principle
Total energy calculations and molecular dynamics simulations employing density functional theory represents a reliable tool to calculate microscopic interaction in condensed matter physics, and material science. The self-consistent all electron calculations for total energy and electronic structure of solids, are being carried out by the first principle computational formalism developed in recent years. A large variety of applications in systems such as different molecules, bulk material and surfaces have proved the power of these methods in analyzing as well as in predicting...
Among these formalism due to Bockstedte et al. [2] offers an elegant and efficient framework for treatment of the defect problems in transition metals. This formalism is based upon the density functional theory, and the calculation of total energy and the Kohn Sham operator in a plan wave basis set is done by momentum space method [3]. The Kohn-Sham density functional equations are solved using iterative schemes of Williams and Solor [4] and Payne et al. [5]. The frozen core electrons are considered by norm conserving pseudopotentials in a fully separable form [6].

The aim of this chapter is to evaluate the atomic forces due to interstitial hydrogen in transition metal host, and subsequently use these forces to evaluate the atomic displacements using discrete lattice static method [7, 8], as the data obtained from these calculations are of vital importance to study the elastic and electronic properties of metal hydrogen solid solutions [9, 10, 11]. The plan of the chapter is as follows: The formalism [2] for calculating external forces using Density functional formalism is given in section 5.2. The computational details of the programme used here are mentioned in section 5.3. The calculations and results are presented in section 5.4 and these are discussed in section 5.6.

5.2 Density functional formalism

The Kanzaki lattice static formalism described in the Chapter-2 has been applied to self-interstitial defect in Chapter-4. The same formalism is used to calculate the lattice distortion due to interstitial hydrogen in Cu and Pd. However, the external forces are calculated using density functional theory. Since the Embedded atom potential is of parameterized form of \textit{ab initio} calculations, therefore involves the fitting to many experimental data, and hence are available only for few transition metals. Therefore more realistic way to study interionic interactions is to calculate
them directly for particular system self-consistently using DFT.

The external force exerted due to interstitial impurity is evaluated self-consistently from the total energy of the defect system \[12\]. For the accurate evaluation of interatomic forces, the electronic structure of the system must be precisely known, which is obtained by solving the many-body Schrödinger equation for host-impurity system.

In order to accomplish that, the many body Schrödinger equation, which is given as follows, must be solved.

\[
H_{MB} = \sum_{\mu} \frac{\hat{p}_{\mu}^2}{2M_{\mu}} + \sum_i \frac{\hat{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i<j} \frac{1}{|r_i - r_j|} - \sum_{\mu} \frac{Z_\mu}{|r_i - \bar{R}_\mu|} + \frac{1}{2} \sum_{\mu>\nu} Z_\mu Z_\nu |\bar{R}_\mu - \bar{R}_\nu|, \tag{5.1}
\]

where \(Z_\mu\) and \(M_\mu\) are ionic charges and masses and \(\hat{p}_\mu\) and \(\hat{p}_i\) are momentum operator for ions and electrons, \(m_i\) is electron mass, \(r_i\) and \(\bar{R}_\mu\) are the electronic and atomic coordinates \(m_i\).

To solve the Equation (5.1), the electronic and ionic motions are decoupled using Born-Oppenheimer approximation i.e.

\[
H_{MB} = \sum_{\mu} \frac{\hat{p}_{\mu}^2}{2M_{\mu}} + \tilde{E}(\{\bar{R}_\mu\}), \tag{5.2}
\]

\[
(H_{MB} - \sum_{\mu} \frac{\hat{p}_{\mu}^2}{2M_{\mu}})\Psi(\bar{R}_\mu)(r_i) = \tilde{E}(\{\bar{R}_\mu\})\Psi(\bar{R}_\mu)(r_i), \tag{5.3}
\]

where \(\tilde{E}(\{\bar{R}_\mu\})\) is the ground state energy of the electron system with frozen ionic configurations (\(\{\bar{R}_\mu\}\)) and \(\Psi(\bar{R}_\mu)(r_i)\) is the many-body electron wave function. The atomic forces can be obtained from the ground state energy by using Hellmann-Feynman theorem \[13\] i.e.

\[
F_\nu = -\frac{\partial\tilde{E}(\{\bar{R}_\mu\})}{\partial \bar{R}_\nu}. \tag{5.4}
\]

The calculation of the ground state energy \(\tilde{E}(\{\bar{R}_\mu\})\), as well as its derivative becomes more accurate and tractable in the mean field theory approach using density

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functional theory (DFT), which is based on Hohenberg-Kohn theorem [14] where following steps are accounted for:

(i) The total energy of a system of interacting electrons can be represented as a functional of electron charge density $\rho(r)$ i.e.

$$
\rho(\vec{r}, \{\vec{R}_e\}) = N_e \int |\Psi_{\{\vec{R}_e\}}(\vec{r}, \vec{r}_2...\vec{r}_{N_e})|^2 d\vec{r}_2...d\vec{r}_{N_e}, \quad (5.5)
$$

where $N_e$ is the number of electrons in the system. Thus $E_{el} = E[\rho(\vec{r})]$ effectively maps the many-electron problem onto a one-electron problem.

(ii) The ground state electron density $\rho_{gs}(\vec{r})$ minimizes the functional $E[\rho(\vec{r})]$ i.e. $E[\rho(\vec{r})] \geq E[\rho_{gs}(\vec{r})].$

The energy $E[\rho_{gs}(\vec{r})]$ represents the electronic part of the total energy $E(\{\vec{R}_e\})$ i.e.

$$
E(\{\vec{R}_e\}) = E[\rho_{gs}(\vec{r})] + \frac{1}{2} \sum_{\mu\nu} \frac{Z_{\mu}Z_{\nu}}{|\vec{R}_\mu - \vec{R}_\nu|}, \quad (5.6)
$$

Here, instead of solving the true many-body Eq.(5.3) in order to find $E(\{\vec{R}_e\})$, we only need to find a minimum of the functional $E[\rho(\vec{r})]$. The cost for this great simplification is that the exact form of the functional $E[\rho]$ is unknown. However this problem can be solved using Kohn-Sham method. The ionic part, is considered through coulomb interactions which are summed up using Ewald $\theta$-function transformation [15].

5.2.1 Kohn-Sham equations

The Kohn-Sham equation[15] is Schrödinger equation, where the potential energy of electrons is formally expressed as functional of electron density. The electronic energy functional $E[\rho(\vec{r})]$ is split into four parts i.e.

$$
E[\rho] = T_e[\rho] + E_{\text{ion}}[\rho] + E_H[\rho] + E_{\text{xc}}[\rho], \quad (5.7)
$$
where $T_e[\rho]$ is the kinetic energy of non-interacting electrons, $E_{\text{ion}}[\rho]$ is the energy of electron-ion interaction i.e.

$$E_{\text{ion}}[\rho] = \int V_{\text{ion}}(r) \rho(r) dr, \quad V_{\text{ion}}(r) = - \sum_{\mu} \frac{Z_{\mu}}{|r - R_{\mu}|} \tag{5.8}$$

where $V_{\text{ion}}(r)$ is electron-ion interaction potential. This is replaced by effective soft pseudopotential, which enables efficient use of a plane wave basis. The pseudopotential for such electronic structure calculation of polyatomic system is calculated by ab initio calculations using DFT, as described in the section 5.2.3.

$E_H[\rho]$ is the energy of classical Hartree electron-electron interaction i.e.

$$E_H[\rho] = \frac{1}{2} \int V_H(\vec{r}) \rho(\vec{r}) d\vec{r},$$

where Hartree potential is

$$V_H(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \tag{5.9}$$

and finally $E_{\text{xc}}(\rho)$ is the term that accounts for electronic exchange and correlation interaction. The exchange energy of electronic system is due to antisymmetry of the wave function, and correlation energy is the difference of many body energy of electronic system and the system studied in Hartee-Fock approximation. The combined expression for exchange-correlation potential is the functional derivative of $E_{\text{xc}}(\rho)$ i.e.

$$V_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\vec{r})} \tag{5.10}$$

$T_e[\rho]$ is the kinetic energy of a system of non-interacting electrons with electron-charge density equal to $\rho(\vec{r})$ i.e.

$$T_e(\rho) = 2 \sum_{i} \langle \phi_i | - \frac{1}{2m} \nabla^2 | \phi_i \rangle \tag{5.11}$$

where $\rho(\vec{r}) = 2 \sum_{i} \langle \phi_i | \phi_i \rangle$ and $\phi_i(\vec{r})$ are the single electron orbitals. Now the variational principle can be used to equation (5.7), since only the minimum value of Kohn-Sham energy functional has physical meaning. At the minimum, the Kohn-Sham energy functional is equal to the ground state energy of the system of electrons.
with ions positions \( \{ \mathbf{R}_i \} \). This results in the set of equations for Kohn-Sham orbital \( \phi_i \), i.e.
\[
[-\frac{1}{2m} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})] \phi_i(\mathbf{r}) = [-\frac{1}{2m} \nabla^2 + V_{\phi}(\mathbf{r})] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \quad (5.12)
\]
where \( \varepsilon_i \) is the Kohn-Sham eigenvalue for orbital \( \phi_i(\mathbf{r}) \) and \( V_{\phi}(\mathbf{r}) \) is the self-consistent potential (effective potential) i.e.
\[
V_{\phi}(\mathbf{r}) = V_{\text{ion}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d^3 r' + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\mathbf{r})}, \quad (5.13)
\]
where \( E_{\text{xc}}(\rho) \) is calculated using Local Density Approximation (LDA). Once the \( E_{\text{xc}}(\rho) \) is evaluated, the Kohn-Sham method gives \( E[\rho_{\text{gs}}(\mathbf{r})] \) and hence the exact value of the ground state energy \( E(\{ \mathbf{R}_i \}) \).

### 5.2.2 Local density approximation

In the local density approximation (LDA), the many-electron problem is approximated by set of single-particle equations which are solved self-consistently. Here the exchange-correlation energy of an electronic system is constructed by assuming that the exchange-correlation energy per electron at a point \( \mathbf{r} \) in the electron gas, \( \varepsilon_{\text{xc}}(\mathbf{r}) \), is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same density as that of the electron gas at the point, thus
\[
E_{\text{xc}}[\rho(\mathbf{r})] = \int \varepsilon_{\text{xc}}(\mathbf{r}) \rho(\mathbf{r}) d^3 r \quad (5.14)
\]
and
\[
\frac{\delta E_{\text{xc}}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} = \frac{\partial[\rho(\mathbf{r}) \varepsilon_{\text{xc}}(\mathbf{r})]}{\partial \rho(\mathbf{r})} \quad (5.15)
\]
with
\[
\varepsilon_{\text{xc}}(\mathbf{r}) = \varepsilon_{\text{xc}}^{\text{hom}}[\rho(\mathbf{r})]. \quad (5.16)
\]
The local-density approximation assumes that the exchange-correlation energy functional is purely local. Several parameterizations exist for the exchange-correlation energy of a homogeneous electron gas [16]. These parameterizations use interpolation formulas to link exact results for the exchange-correlation energy of high-density
electron gases and calculations of the exchange and correlation energy of intermediate and low-density electron gases.

5.2.3 Ionic pseudopotential

The pseudopotential is used in the total energy calculations in DFT, to simplify the interactions with core electrons. One uses the fact that for most of the atomic species the core electrons only weakly participate in the chemical bonding in the solid, and thus their contributions can be approximated by smooth and slow varying potential, which increases the efficiency of computations.

The computational procedure for generating pseudopotential is shown in the flow chart in Fig.5.2 and the brief theoretical description is discussed here briefly. We use scheme by Hamman [17], to construct screened norm conserving pseudopotential by solving non relativistic Schrödinger equation.

\[
\left[ \frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_{l}^{\text{ps,scr}}(r) - \epsilon_{l}^{\text{ps}} \right] u_{l}^{\text{ps}}(\epsilon_{l}^{\text{ps}}; r) = 0, \quad (5.17)
\]

where the radial pseudo wavefunction \( u_{l}^{\text{ps}}(r) \) is derived from the all electron valence levels with angular momentum \( l \).

The pseudo wavefunction and all-electron wavefunction correspond to the same eigenvalue and their logarithmic derivative agree beyond a chosen core cutoff radius \( r_c \). The radial pseudo wavefunction has the same amplitude as the all electron wavefunction beyond the core cutoff radius. The pseudo wavefunction contains no radial nodes and \( V_{l}^{\text{ps,scr}} \) is the screened pseudopotential.

The screened pseudopotential components \( V_{l}^{\text{ps,scr}} \) then correspond to an inversion of the Schrödinger Eq.(5.17) for the respective pseudo wavefunction as

\[
V_{l}^{\text{ps,scr}}(r) = \epsilon_{l}^{\text{ps}} - \frac{l(l+1)}{2r^2} + \frac{1}{2\epsilon_{l}^{\text{ps}}(r)} \frac{d^2}{dr^2} u_{l}^{\text{ps}}(r), \quad (5.18)
\]
The ionic norm-conserving pseudopotential is determined by subtracting from the screened pseudopotential the electrostatic and the exchange-correlation screening contributions due to valence electrons i.e.

\[ V_{\text{ion}}^{\text{val}}(r) = V_{\text{ion}}^{\text{PAW}}(r) - V^H[\rho_0^v; r] - V^{XC}[\rho_0^v; r] \]

with

\[ \rho_0^v(r) = \frac{1}{4\pi} \sum_{i=0}^{i_{\text{max}}} \int |u_i^{\text{PAW}}(r)|^2. \]  

The valence electron density \( \rho_0^v(r) \) is evaluated from the atomic pseudo wavefunc-
tions, with the same occupancies $f_i$. The pseudopotentials are represented in the fully separable form as proposed by Kleinman and Bylander [18], which is given as

$$V_{0s}^{ps} = V_{0s,loc} + \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \frac{\left| \Delta V_{0s}^{nl} \right| V_{0s,loc}^{nl} \left( \Delta V_{0s}^{nl} \right)}{V_{0s,loc}^{nl} \left( \Delta V_{0s}^{nl} \right)}, \quad (5.20)$$

where $\Delta V_{0s}^{nl}(r) = V_{0s}(r) - V_{0s,loc}(r)$, and $V_{0s}(r)$ are radial components of the semi-local pseudopotential, $V_{0s,loc}(r) = V_{0s}^{nl}(r)Y_l^m(\theta, \phi)$ are the node free atomic pseudo wavefunctions. In this form the pseudopotential is split into a local part $V_{0s,loc}$ and a nonlocal but separable part $V_{0s,nl}$. Correspondingly the potential is expressed as

$$V_{0s}^{ps} = V_{0s,loc} + V_{0s,nl}. \quad (5.21)$$

The computational details for evaluation of pseudopotential are described in the section-5.3.

### 5.3 Computational details

The external force due to interstitial hydrogen in transition metal, is calculated from total energy of the system using Hellmann-Feynman theorem [13]. For calculating total energy of the system having defect, central quantities are, the ionic interaction $V_{ion}$ and arrangement of defect in the system. The ionic interactions are considered through norm conserving pseudopotential in a fully separable form [18]. The transferability of the pseudopotential is examined by examining scattering properties by taking logarithmic derivative at the core cutoff radius, and calculating the excitation energies of the free pseudo atom.

The ionic pseudopotential for H, Cu, and Pd is generated using the ab initio method [6] as described in the section 5.2.3. The hydrogen pseudopotential is calculated in scalar-relativistic mode, with number of valence states= 1, and $l_{max} = 1$. The core cutoff radius for hydrogen is $r_{cut} = 0.78$ a.u.. The variation of the ionic
Figure 5.3: Ionic pseudopotential for Hydrogen (a.u.) calculated using density functional theory.

The pseudopotential involving only s wave function is shown in the Fig.5.3. The potential shows minima at $r=0.3$ a.u. and becomes nearly constant beyond $r=5$ a.u.

For Cu pseudopotential, we use $Z=29.0$, valence electrons=11, core states = 5, valence states= 2, $l_{\text{max}} = 3$ and core cutoff radius is fixed at $r_{\text{cut}} = 2.1$ a.u. The variation of s, p, and d components of norm-conserving ionic potential are shown in Fig.5.5. s,p components are small and nearly constant while d component is strongly attractive and shows minima at about $r=0.2$ a.u.. Cu ionic pseudopotential becomes nearly constant for $r > 2$ a.u.

For Pd pseudopotential calculation, we use $Z=46.00$, valence electrons=10, core states=8, valence states=2, $l_{\text{max}} = 3$ and $r_{\text{cut}}=3.15$ a.u.. The variation of s, p, and d components of norm-conserving ionic potential are shown in Fig.5.6. It is interesting
to note that the ionic pseudopotential for Pd is not the same as for Cu. The s component has minimum at r=1.5 a.u., while p-component is increasing steadily. The d-component has the broad minima at r=0.7 a.u. and the potential becomes constant at large distance. The pseudopotential for Pd ions is weaker than the Cu ion. The pseudopotential for Cu is short ranged as components to the pseudopotential for hydrogen and Pd ion. Interestingly the hydrogen pseudopotential is feeble but long ranged and extending its effect to far distant host atom. The exchange-correlation interactions are considered through LDA [16] while calculating the pseudopotential.
For electronic structure calculations, the geometry of the atomic structure of the system (interstitial hydrogen in fcc lattice) is defined through structure factor. We consider the cluster of $M_{32}H$ shell (where $M = \text{Cu}$ and Pd) as shown in Fig.5.1, for total energy calculation using Eq.(5.6) and evaluating force using Eq.(5.4). Since atomic forces at the fixed lattice points are required to evaluate the atomic displacements due to interstitial hydrogen in the discrete lattice model. Therefore these are not allowed to relax i.e. the position of the atoms are kept fixed while calculating the forces at the required positions. For solving Eq.(5.6), we use the computational procedure developed by Bockstedte et al [2]. The computational sequence is shown in the flow chart shown in Fig.3.4 for total energy calculation. The exchange-correlation
energy are evaluated using local density approximation (LDA) with the same set of parameters as used to generate pseudopotential [16].

The initial wave functions $|\phi_{ik}^0>$ are calculated by explicit diagonalization of the Kohn-Sham operator in the mixed basis set. After each iteration step the wavefunction $|\phi_{ik}>$, have to be ortho-normalized, which is done by Gram-Schmidt scheme. We use energy cutoff limit for plane waves as $E_{cut}=12$ Ry and for energy cutoff of the initial wave function $E_{cut_i}=8$ Ry. The damped Joannopoulos algorithm [19] is used for wave function iteration to minimize the energy of the system, with 100 self consistent iteration cycles to obtain convergence.
5.4 Calculations and results

We use discrete lattice method to calculate the lattice distortion around interstitial hydrogen in Cu and Pd. The central quantity in the evaluation of strain field due to interstitial hydrogen is the interatomic forces between host metal surrounding a hydrogen atom. These forces are calculated from total energy of $M^H$ ($M=\text{Cu, Pd}$) shell using Eq.(5.4), details for which are presented in the sections 5.2, and 5.3. The force constants $A_1$ and $B_1$ calculated in the Chapter-3 are also used in present calculation given in the Table 5.1 along with external force at 1NN's and 2NN's. These calculated values of $F_1$, $F_{1i}$, $A_1$ and $B_1$, are used to calculate $\phi_{ab}(q)$ and hence $\bar{Q}(q)$, with the help of Eq.(2.13). The inverse Fourier transform of $\bar{Q}(q)$, as given in Eq.(2.7), gives $\vec{u}(R_0)$. The numerical integration inscribes the first Brillouin zone (BZ) is carried using Eq.(3.17).

The atomic displacements of 22NN’s due to interstitial hydrogen at octahedral site in Cu and Pd are given in Tables 5.2-5.3. The nature of the atomic displacements of NN’s for Cu and Pd is the same. The first 4NN’s of hydrogen move away from the hydrogen, and fifth NN’s show contraction towards the hydrogen atom. Than again 4NN’s move away from hydrogen and fifth towards hydrogen. Over only few NN move towards the impurity and most of them move away from the impurity. Although the displacements are oscillatory in nature but decreases in magnitude with increasing NN’s distance. The maximum displacements is at 1NN’s of hydrogen and Cu atoms are displaced more than Pd atoms.

The maximum displacement of 7.6% and 4.9% of 1NN distance is found at the 1NN’s of hydrogen in Cu and Pd respectively in our calculation. As these atomic displacements are significantly up to first few NN’s only. Thus hydrogen causes significant lattice expansion due to its interstitial location, the volume change is calculated considering the displacements up to 2NN’s of the hydrogen atom. The calculated fractional relative change in the volume ($\delta V$) is 0.169 and 0.107 for CuH.
Table 5.1 The physical parameters (in a.u.) for Cu and Pd metals. \(a\) is the lattice constant, \(Z\) is the number of electrons in the outer orbit, and \(A_i\) and \(B_i\) are force constants and \(F_i\) and \(F_{II}\) (a.u.) are hydrogen induced forces at the first and second nearest neighbors of hydrogen impurity. \(E_r\) is hydrogen induced relaxation energy.

<table>
<thead>
<tr>
<th>Host</th>
<th>(a)</th>
<th>(Z)</th>
<th>(A_1)</th>
<th>(B_1)</th>
<th>(F_I)</th>
<th>(F_{II})</th>
<th>(-E_r)(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>6.82</td>
<td>11</td>
<td>0.01567</td>
<td>-0.0035</td>
<td>0.0269</td>
<td>0.0013</td>
<td>0.076</td>
</tr>
<tr>
<td>Pd</td>
<td>7.35</td>
<td>10</td>
<td>0.0400</td>
<td>-0.0094</td>
<td>0.0372</td>
<td>0.0025</td>
<td>0.067</td>
</tr>
</tbody>
</table>

and PdH system. The experimental value of fractional change in volume for PdH system are found in the range of 0.20 to 0.13 for different concentration of hydrogen in Pd, with average value 0.19±0.01 [20]. These numbers are in reasonable qualitative agreement. The volume change for \(Pd_{32}H\), estimated from the trace of the dipole tensor [1] are in close agreement with the result presented here.

The calculated atomic displacements up to 2NN's are used to calculate the hydrogen induced relaxation energy \(E_r\) as given in Eq(2.46). The relaxation energies due to interstitial hydrogen in Cu and Pd are -0.076eV and -0.067eV respectively. Therefore hydrogen is easily solvable in Pd than in Cu.
Table 5.2 Atomic displacements (a.u.) of the NN’s of Hydrogen at the octahedral site in the Cu. ($n_1, n_2, n_3$) (in a/2 units) are coordinates of the NN’s of hydrogen and ($u_x, u_y, u_z$) are the Cartesian components of the atomic displacements.

| ($n_1, n_2, n_3$) | $u_x$  | $u_y$  | $u_z$  | $|u|$ |
|-------------------|--------|--------|--------|------|
| 100               | 0.3552 | 0.0000 | 0.0000 | 0.3552 |
| 111               | 0.0159 | 0.0159 | 0.0159 | 0.0275 |
| 210               | 0.0554 | 0.0699 | 0.0000 | 0.0891 |
| 221               | 0.0270 | 0.0270 | 0.0294 | 0.0482 |
| 300               | -0.0391| 0.0000 | 0.0000 | 0.0391 |
| 311               | 0.0106 | 0.0214 | 0.0214 | 0.0321 |
| 320               | 0.0219 | 0.0328 | 0.0000 | 0.0394 |
| 331               | 0.0206 | 0.0206 | 0.0144 | 0.0325 |
| 333               | 0.0214 | 0.0214 | 0.0214 | 0.0371 |
| 410               | -0.0232| -0.0004| 0.0000 | 0.0233 |
| 421               | 0.0051 | 0.0130 | 0.0069 | 0.0155 |
| 430               | 0.0122 | 0.0182 | 0.0000 | 0.0219 |
| 432               | 0.0164 | 0.0171 | 0.0129 | 0.0270 |
| 441               | -0.0017| -0.0024| -0.0011| 0.0031 |
| 443               | 0.0146 | 0.0146 | 0.0060 | 0.0215 |
| 520               | 0.0160 | 0.0160 | 0.0135 | 0.0264 |
| 522               | -0.0114| -0.0005| 0.0000 | 0.0114 |
| 533               | 0.0000 | 0.0043 | 0.0043 | 0.0061 |
| 540               | 0.0102 | 0.0099 | 0.0099 | 0.0173 |
| 544               | 0.0086 | 0.0117 | 0.0000 | 0.0145 |
| 630               | 0.0122 | 0.0109 | 0.0109 | 0.0196 |
| 641               | -0.0058| 0.0004 | 0.0000 | 0.0059 |
Table 5.3. Atomic displacements (a.u.) of the NN’s of Hydrogen at the octahedral site in the Pd. \((n_1, n_2, n_3)\) (in \(\alpha/2\) units) are coordinates of the NN’s of hydrogen and \((u_x, u_y, u_z)\) are the Cartesian components of the atomic displacements.

| \((n_1, n_2, n_3)\) | \(u_x\)  | \(u_y\)  | \(u_z\)  | \(|u|\) |
|---------------------|---------|---------|---------|-------|
| 100                 | 0.2254  | 0.0000  | 0.0000  | 0.2254|
| 111                 | 0.0104  | 0.0104  | 0.0104  | 0.0180|
| 210                 | 0.0355  | 0.0340  | 0.0000  | 0.0491|
| 221                 | 0.0125  | 0.0125  | 0.0111  | 0.0208|
| 300                 | -0.0021 | 0.0000  | 0.0000  | 0.0021|
| 311                 | 0.0113  | 0.0086  | 0.0086  | 0.0166|
| 320                 | 0.0131  | 0.0145  | 0.0000  | 0.0195|
| 331                 | 0.0085  | 0.0085  | 0.0049  | 0.0129|
| 333                 | 0.0066  | 0.0066  | 0.0066  | 0.0114|
| 410                 | -0.0004 | 0.0019  | 0.0000  | 0.0020|
| 421                 | 0.0058  | 0.0057  | 0.0031  | 0.0087|
| 430                 | 0.0066  | 0.0072  | 0.0000  | 0.0098|
| 432                 | 0.0061  | 0.0057  | 0.0044  | 0.0094|
| 441                 | -0.0005 | -0.0004 | -0.0002 | 0.0007|
| 443                 | 0.0053  | 0.0053  | 0.0021  | 0.0078|
| 520                 | 0.0047  | 0.0047  | 0.0039  | 0.0077|
| 522                 | 0.0007  | 0.0019  | 0.0000  | 0.0021|
| 533                 | 0.0032  | 0.0026  | 0.0026  | 0.0048|
| 540                 | 0.0042  | 0.0032  | 0.0032  | 0.0062|
| 544                 | 0.0039  | 0.0040  | 0.0000  | 0.0056|
| 630                 | 0.0035  | 0.0029  | 0.0029  | 0.0054|
| 641                 | 0.0012  | 0.0014  | 0.0000  | 0.0018|
5.5 Discussion and summary

The interstitial alloys are unique and the strain held due to these defects has been constrained due to non-availability of reliable interatomic potential at host-interstitial distance. The Density functional theory provided reliable method of calculating total energy and hence the atomic forces. Here the exchange and correlation effects of electrons, are included explicitly and calculated self-consistently. The norm-conserving ionic pseudopotential are generated in separable form to calculate the total energy. The transferability of the pseudopotential has been examined by examining scattering properties, excitation energies, and chemical hardness properties of the free pseudo atom.

Here we considered M32H shell (M = Cu and Pd), due to computational limitations. As the effective pseudopotential are extended up to \( r = 5.0 \) a.u., therefore the considerations of forces up to 2NN's does not introduce any serious error. The cluster considered is not allowed to relax i.e. fixed coordinates, this is in accordance with our formalism to calculate strain field, as we need forces at the fixed atomic sites. The reasonable agreement of the fractional volume change calculated from tabulated displacements and the experimental value, shows that the interaction of the interstitial defects in alloys are effectively described using density functional theory.

The large displacements caused due to interstitial hydrogen in Cu and Pd, needs careful investigation, before considering technological use of such interstitial alloys in hydrogen environment. Further, the calculated displacements are of vital importance for the calculation of electric field gradient, heat of solution, knight shift, wipe out number and other important physical properties where displaced positions of Cu and Pd atoms due to hydrogen are needed.
Bibliography


