CHAPTER 2: THEORETICAL METHODOLOGY

The electrons and nuclei are the determining factor for understanding the properties of condensed matter and molecules. It provides us information about the electronic, optical, magnetic and bulk properties of the material. An accurate determination of the electronic structure of the molecule is an important factor as it dominates the properties of the whole system. In the last few decades, experimentalist and theoreticians have been studying these properties for various scientific and technological applications. However due to complexity of the condensed matter systems, experimentally studying these properties under extreme conditions of pressures and temperature is tedious and difficult work. Theoretical study often provides a good understanding of the physics of the system under study, and it is often possible to interpolate or extrapolate these models in order to predict the behavior of systems under conditions not yet tested experimentally. Also developments in computational simulation have made it possible to study properties of materials from the first principle calculation with great accuracy. Thus it enables the explanations and prediction of the materials properties which are difficult to study experimentally. Various electronic structure methods have been developed in the past and modern physics is always faced with a challenge to develop computational methods that will accurately treat the interacting system of many electrons and nuclei.

2.1. Many body problem

The behaviour of interacting electrons in a solid is very difficult to understand and is a tremendous task which can only be addressed partially. This is not due to purely theoretical reasons but also to numerical reasons. Computers have become more and more powerful allowing physicists to solve more and more complex problems. However, the interacting-electron problem has been known for more than 80 years and despite the advent of computers and supercomputers, this particular task is still out of reach.

Solving the many-body Schrodinger equation is the starting point for investigating the properties of a material but the number of particles that are involved and the coupling and interactions of the particles cause a problematic issue which can be overcome by using approximation methods.

In a solid system, there are nuclei and electrons. For a solid, the Hamiltonian of the system of nuclei and electrons can be written as

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \qquad (2.1)$$

where, $\hat{H}$ is the Hamiltonian for the system consisting of M nuclei and N electrons. The sum over A and B runs over the M nuclei while the sum over i and j run over the N electrons. M_A and Z_A are the mass and atomic number of Ath nucleus, r_{iA} is the distance with A^{th} nucleus and i^{th} electron, r_{ij} represents the distance between i^{th} and j^{th} electrons, R_{AB} is the distance between A^{th} and B^{th} nuclei. Atomic units in which $\hbar = m = e = 1$, are used throughout the thesis work.

The first term is the kinetic energy for the electrons and second term is for the nuclei. The last three terms represents the attractive electrostatic (coulomb) interaction between the electrons and the nuclei and repulsive potential due to the electrons and nucleus-nucleus interaction respectively. Solving this problem is impossible, therefore acceptable approximate eigenstates is found out by making approximations at three levels.

2.2. Born-Oppenheimer approximation

We know that nuclei are much heavier and slower than electrons; we can therefore freeze them at fixed points and assume that only electrons are moving. Now since the nuclei do not move anymore, the kinetic energy becomes zero and the potential energy due to nucleus-nucleus interactions become constant. Thus we are left with three terms: the kinetic energy of the electron, the potential due to

the electron-electron interaction and the potential energy of the electrons in the external potential of the nuclei.

Now the above equation becomes

$$\widehat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i-1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} \qquad (2.2)$$

which can be formally written as

$$\widehat{H} = \widehat{T} + \widehat{V}_{ee} + \widehat{V}_{ext} \qquad (2.3)$$

where

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2$$

$$\hat{V}_{ee} = \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

$$\hat{V}_{ext} = -\sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}}$$

The kinetic and the electron-electron terms of the above equation (2.3) depends only on the fact that we are dealing with a many-electron system and are independent of the solid system.

2.3. Density functional theory (DFT)

The Hamiltonian obtained after Born-Oppenheimer approximation is much simpler than the original Hamiltonian. But it is still difficult to solve. There are several methods to reduce equation (2.3) to an approximation but tractable form. One important approximation is the *Density Functional Theory (DFT)*.

Density-functional theory (DFT) is one of the most widely used technique in condensed matter physics and quantum chemistry [53,54,55] employed to study the ground state properties calculation of atoms, molecules or solids. It is first principle theory of condensed matter physics for the electron-electron many-body problem through the introduction of an exchange-correlation term in the

functional of the electronic density. It is a very reliable theory for predicting new materials, to confirm experimental discoveries, or to provide explanation of new phenomena observed in experimental work.

DFT is the quantum mechanical approach for solving the many electron system. It is based on the electronic density distribution rather than the many electron wave functions and transforms the many body system into a system of non-interacting fermions in an effective field called Kohn –Sham equation.

The Density Functional Theory concept for atomic spheres was first introduced by Thomas and Fermi around 1927-1928 [56,57] with further improvements by Hartree [58], Dirac [59, 60], Fock [61] and Slater [62] but the formal establishment of DFT was given by Hohenberg and Kohn [63] in 1964.

Hohenberg and Kohn gave two theorems mainly known as the Hohenberg-Kohn theorem. This theorem enables us to establish a unique correspondence between the external potential and ground state density.

2.3.1. Hohenberg and Kohn theorem

Theorem 1: The ground state electron density of a system determines the external potential $V_{ext}(r)$ (within a trivial additive constant). In other words there is one to one correspondence between the ground state density, $\rho(r)$ and the external potential $V_{ext}(r)$.

Theorem 2: The density that minimises the variational energy is the true ground state density for the external potential, V_{ext} i.e. the total energy functional has a minimum equal to the ground state energy at the ground state density of the system.

(The proofs of theorem 1 and theorem 2 are given in appendix B)

2.3.2. Kohn Sham Equation

In 1965 Kohn-Sham gave a proposal which reduced the long task of dealing with many particle Schodinger equation for real system to a relatively easy to solve set of one particle equations of a virtual system [64].

Hohenberg and Kohn proved that the ground state energy can be written as a unique functional of the electron density.

Therefore the total energy of an interacting system is

$$E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ext}[\rho] \tag{2.4}$$

Now we can consider a virtual system of non-interacting electron system of same density ρ having the same energy functional $E[\rho]$ with the original system, then rearranging the terms, we can write as

$$E[\rho] = T_S[\rho] + E_{Hartree}[\rho] + E_{ext}[\rho] + \{T[\rho] - T_S[\rho] + E_{ee}[\rho] - E_{Hartree}[\rho]\} \tag{2.5}$$

where $T_s[\rho]$ is the non-interacting kinetic energy corresponding to density ρ. The kinetic energy functional $T[\rho]$ has been replaced by the non-interacting kinetic energy term $T_s[\rho]$.

$E_{Hatree}[\rho]$ is the Hatree energy which is the usual classical coulomb interaction as a functional of density ρ. Therefore the energy functional remains the same. The first three terms in the above expression are the major terms quantitatively and can be treated exactly.

The last term,

$$\{T[\rho] - T_S[\rho]\} = E_C[\rho] \ , \{E_{ee}[\rho] - E_{Hatree}[\rho]\} = E_X[\rho]$$

$$\{T[\rho] - T_S[\rho] + E_{ee}[\rho] - E_{Hartree}[\rho]\} = E_C[\rho] + E_X[\rho] = E_{XC}[\rho]$$

is called exchange correlation energy.

It is about 10% of the total energy. Therefore an approximation of reasonable accuracy is acceptable for this part as far as energy calculation is concerned. It is this part which draws most of the attention of DFT researchers.

Now the kinetic energy functional of the non-interacting electron system $T_s[\rho]$ is expressed as,

$$T_S[\rho] = -\frac{1}{2}\left\langle \psi_S[\rho]\middle|\nabla^2\middle|\psi_S[\rho]\right\rangle \tag{2.6}$$

where ψ_S is Slater determinant formed from single particle orbitals $\phi_i's$. It is given as,

$$\psi_s = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_{N-1}) & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_{N-1}) & \phi_2(x_N) \\ \vdots & \vdots & \cdots & \vdots & \vdots \\ \phi_{N-1}(x_1) & \phi_{N-1}(x_2) & \cdots & \phi_{N-1}(x_{N-1}) & \phi_{N-1}(x_N) \\ \phi_N(x_1) & \phi_N(x_N) & \cdots & \phi_N(x_{N-1}) & \phi_N(x_N) \end{vmatrix} \tag{2.7}$$

The ground state electron density is then given by

$$\rho(r) = \sum_i |\phi_i(r)|^2 \tag{2.8}$$

Thus,

$$E[\rho] = -\frac{1}{2}\sum_i\left\langle \phi_i[\rho]\middle|\nabla^2\middle|\phi_i[\rho]\right\rangle + \frac{1}{2}\iint\frac{\rho(r)\rho(r')}{|r-r'|}drdr' + \int v_{ext}\rho dr + E_{XC}[\rho] \tag{2.9}$$

Minimising the above expression for energy with respect to the orbital's and using the condition $\int|\phi_k(r)|^2 dr = 1$ we get,

$$\left[-\frac{1}{2}\nabla^2 + \int \frac{\rho(r')}{|r - r'|} dr' + v_{ext}(r) + v_{XC}(r) \right] \phi_k = \varepsilon_k \phi_k \qquad (2.10)$$

This equation is DFT counterpart of Schrodinger equation and is known as the Kohn-Sham equation. Here ϕ_k's are the Kohn-Sham orbital's and ε_k's enter into the equation as Lagrange undetermined multiplier and are the Kohn-Sham orbital energies. v_{ext} and v_{XC} are respectively, external potential and the exchange correlation potential.

Total energy of the system is also expressed as,

$$E[\rho] = \sum_{k=1}^{N} \varepsilon_k - \frac{1}{2}\iint \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' - \int v_{ext}\rho(r) dr + E_{XC}[\rho] \qquad (2.11)$$

The Kohn-Sham calculation proceeds as follows. At first we start with an initial density $\rho(r)$ and solve the Kohn-Sham equation self-consistently to generate a set of Kohn-Sham orbitals from which then we calculate ground state total energy as a functional of ground state density.

(Detailed mathematical steps of this calculation is given in appendix C)

2.4. Approximations to exchange correlation potential

Exchange correlation potential is obtained as the functional derivative of the exchange correlation energy as,

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)} \qquad (2.12)$$

In practice, exchange correlation energy is split into exchange and correlation part separately. Therefore we have,

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \tag{2.13}$$

Corresponding potentials are also defined separately as, $v_x(r) = \dfrac{\delta E_x[\rho]}{\delta \rho(r)}$ and

$v_c(r) = \dfrac{\delta E_c[\rho]}{\delta \rho}$. Exchange part constitutes about 10% of the total energy while correlation part constitutes less than one percent of the total energy for the majority systems. Correlation effects, although small become important in certain cases such as information of negative ions. Therefore it is very important that accurate exchange and correlation energy functional be available for density functional calculations.

There are different types of approximations involved in DFT calculation for the unknown exchange-correlation density functional $E_{XC}[\rho]$ which make DFT practically implementable. The approximations are Local Density Approximation (LDA), Generalised Gradient Approximation (GGA) and Generalised Density Approximation with modified Becke Johnson (GGA+mbJ).

2.4.1. Localised Density Approximation (LDA)

The Local Density Approximation (LDA) also known as the local functional proposed by Kohn and Sham in 1965 and is the basis of all approximate exchange-correlation function. In LDA one assumes that the exchange correlation energy leads to an exchange correlation potential depending on the value of density in 'r' and not on its gradient.

$$E_{XC} = \int \rho(r) \varepsilon_{xc}[\rho(r)] dr \tag{2.14}$$

where ε_{xc} is the exchange-correlation energy density of the uniform electron gas of density $\rho(r)$ [65]. It is exact for a homogenous electron gas so it works well for systems in which the electron density does not vary too rapidly. The LDA

functional reproduces the ground state properties of many systems very accurately. They are also known to predict inaccurately the energy band gap of semiconductor materials [66,67,68].

2.4.2. Generalised Density Approximation (GGA)

Besides the local density approximation (LDA), a number of non-local approximations have been suggested. The reason for that is a high value of density gradient in some materials. But even when the gradient is not small the LDA gives good results. The approximation which accounts for spatial variation of density is usually termed as the Generalised Gradient Approximation (GGA). In GGA the gradient of the charge density is included in the exchange-correlation functional in order to account for the non-homogeneity of the true electron density i.e. the exchange correlation potential is a function of both the charge density at a given point and the first order gradient of the charge density at the same point.

$$E_{XC}[\rho] = \int \rho(r)\varepsilon_{xc}(\rho(r)\nabla\rho(r))d^3r \qquad (2.15)$$

Generally, GGA has the following advantages over LDA [69, 70, 71]:

1. GGA improves ground state properties for light atoms, molecules and clusters.

2. GGA predicts the correct magnetic properties of 3d transition metals such as body centred iron.

There are different types of GGA functional and detailed discussions on the different types of GGA functionals are present in the reference [72].

2.4.3. Generalised Density Approximation with modified Becke Johnson (GGA+mBJ)

The Generalised Density Approximation with modified Becke Johnson (GGA+mBJ) overcomes the underestimation in the calculation of energy band

gaps within the LDA and GGA and competes in accuracy with the expensive hybrid and GW methods. The modified Becke Johnson potential was proposed by Tran and Blah in 2009 [73]. It is a semi local approximation to an atomic "exact-exchange" potential and a screening term. In the modified Becke Johnson potential,

$$\upsilon_{x,\sigma}^{mBJ}(r) = c\,\upsilon_{x,\sigma}^{BR}(r) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{6}}\sqrt{\frac{t_{\sigma}(r)}{\rho_{\sigma}(r)}} \tag{2.16}$$

where $\rho_{\sigma} = \sum_{i=1}^{N_{\sigma}}\left|\psi_{i,\sigma}\right|^2$ is the electron density,

$$t_{\sigma} = \left(\frac{1}{2}\right)\sum_{i=1}^{N_{\sigma}}\nabla\psi_{i,\sigma}^{*}.\nabla\psi_{i,\sigma}$$ is the kinetic energy density,

$$\upsilon_{x,\sigma}^{BR}(r) = -\frac{1}{b_{\sigma}(r)}\left(1 - e^{-x_{\sigma}(r)} - \frac{1}{2}x_{\sigma}(r)e^{-x_{\sigma}(r)}\right)$$ is the Becke-Roussel (BR)

exchange potential [74] which was proposed to model the coulomb potential created by the exchange hole and $\sqrt{\dfrac{t_{\sigma}(r)}{\rho_{\sigma}(r)}}$ is the screening term. In equation (2.16),

$$c = \alpha + \beta\left(\frac{1}{V_{cell}}\int_{cell}\frac{\left|\nabla\rho(r')\right|}{\rho(r')}d^3r\right)^{\frac{1}{2}}$$ i.e. for any value of c, the exchange

potential is obtained for constant electron density. Here V_{cell} is the unit cell volume and $\alpha = -0.012$ and $\beta = 1.023$ bohr$^{1/2}$ are the two free parameters.

This semi local exchange potential, which recovers the local-density approximation (LDA) for a constant electron density, mimics very well the behaviour of orbital-dependent potentials and leads to calculations which are

barely more expensive than LDA calculations and can be applied to very large systems in an efficient way.

2.5. Concepts of Phase Transition.

During a phase transition, certain properties of a given medium often discontinuously changes due to some external conditions such as temperature, pressure and others. These changes of phase are called phase transitions and the phenomena are very important not only in natural processes, but also in industry. In early years the rate at which the transition occurred were observed in attempting the classification of phase transition in solid states. Based on different characteristics of transition, three types of approaches are used for describing phase transition namely the kinetic approach, the thermodynamic approach and the structural approach.

Kinetic approach gives in consideration the transition rate and the activation energy between polymorphs of a given compound. In the thermodynamic approach the changes in the Gibbs free energy as a function of external parameters like temperature, pressure, magnetic field, or electric field are investigated. Lastly in structural approach the structures of the polymorphic phases before and after the transformation are compared. In general, the distinction between transformation types is open to more than one definition and is related to a phenomenological rather than an atomistic understanding of the transition.

In nature, structural phase transitions are common phenomena that can be induced by pressure or temperature. It plays an important role in the discovery of new phases with different chemical and physical properties in solid states. Transformations on increasing pressure often lead to crystalline polymorphs with a defined symmetry because of volume restriction. The basic problems about phase transformations, crystal structure and the nature of atomic bonding can be answered using high-pressure techniques. Also the use of high pressure to

synthesize new materials, to study the behaviour of existing materials and to tune materials physical properties provides tremendous potential for advancement in applied materials research.

There are various observable which characterize the energy aspect of a system. The internal energy U which is the total energy of the system is conserved. The enthalpy $H(=U+PV)$ is the energy needed for creation or destruction of the system with volume V in an environment at a fixed pressure P. As the enthalpy can be used to characterize the heat, the aspects of work can be characterized by the free energy.

The Gibb's free energy is defined as

$$G = U + PV - TS \tag{2.17}$$

In the present study the structural phase transformation from the zinc blende to the rock salt phase is studied. The structural phase transition from ZB to RS (B3→B1) phase is determined by calculating the Gibbs free energy G. Since our calculation is done at zero temperature we have ignored the entropy contribution. Therefore the structural phase transition has been calculated from the condition of equal enthalpies i.e. H=E+PV.

2.6. Theory of Elastic Constants.

The elastic constant of solids provides a link between the mechanical and dynamical behaviours of a crustal and also gives significant information concerning the nature of forces in solids.

Solids are not perfectly rigid and therefore when proper forces are applied, there is change in the shape and size of the material. After the removal of the forces if the changes are not too large, the bodies regain their original shape and size. This property of solid by virtue of which they regain their original shape and size is called elasticity. When an external force is applied to a body in which one part

exerts a force on the neighbouring parts it is known as stress. The elastic constant of a material can represent the deformation of materials under any small stress. According to the linear theory of elasticity strain (relative elongations and distortion) are linearly proportional to the applied stress within the elastic limit of the body. Outside this elastic limit a non linear effects break the proportionality between the stress and strain and for large stresses the deformation becomes irreversible.

The stress and strain of a material are linearly connected by the generalised Hooke's law,

$$\sigma_{mn} = C_{mnpr}\varepsilon_{pr} \tag{2.18}$$

where σ_{mn} is the stress tensor along with the individual elements which are called the stress components, C_{mnpr} are the elastic constants or the stiffness tensor popularly known as the stiffness matrix and ε_{pr} is the strain tensor with its individual elements known as the strain components. Here, m, n, p, r = 1,2, 3.

The stiffness coefficients for this linear stress-strain relationship are the individual elements and therefore the stress and strain tensor has 3×3 = 9 components each while the stiffness tensor has 3^4 = 81 independent elements. These individual elements are referred by various names as elastic constants, elastic moduli and stiffness coefficients and they are the fundamental parameters providing detailed information on the materials mechanical properties. A proper knowledge of these parameters enables us in understanding various mechanical behaviour of the material at different conditions. The number of these elastic constants can be reduced from different symmetries.

Under the stress symmetry, the stress components are symmetric. i.e. $\sigma_{mn} = \sigma_{nm}$ and therefore the nine stress components is reduced to six components only.

Thus equation (2.18) can be written as

$$\sigma_{nm} = C_{nm\,pr}\varepsilon_{pr} \qquad (2.19)$$

Now, subtracting equation (2.19) from (2.18) we get,

$$\sigma_{mn} - \sigma_{nm} = \varepsilon_{pr}\left(C_{mnpr} - C_{nmpr}\right)$$

i.e. $C_{mnpr} = C_{nmpr}$ \qquad (2.20)

There are six independent ways to express m and n taken together and still nine independent ways to express p and r taken together. Thus with this symmetry the number of independent elastic constants reduces to (6×9=) 54 from 81.

Under the strain symmetry the strain components are symmetric. i.e. $\varepsilon_{pr} = \varepsilon_{rp}$. Therefore from equation (2.18),

$$\sigma_{mn} = C_{mnrp}\varepsilon_{rp} \qquad (2.21)$$

Again, subtracting equation (2.20) from (2.19) we get,

$$C_{mnpr} = C_{mnrp} \qquad (2.22)$$

Thus we find from equation (2.20) and equation (2.21) that there are six independent ways of expressing m and n when p and r are fixed and six independent ways of expressing p and r when m and n are fixed. Hence there are 6×6=36 independent constants with stress and strain symmetry.

Thus in matrix format the stress-strain relation showing the 36 independent components of stiffness can be represented as

$$
\begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix}
\tag{2.23}
$$

$$
\sigma_m = C_{mn}\varepsilon_n \quad (m,\ n=1, 2, \ldots, 6)
\tag{2.24}
$$

Now, if we consider the Strain energy density function W, then

$$
W = \frac{1}{2} C_{mn}\varepsilon_m\varepsilon_n
\tag{2.25}
$$

where $\sigma_i = \dfrac{\partial W}{\partial \varepsilon_i}$
$\tag{2.26}$

We see that W is quadratic function of strain and thus can be also written as

$$
W = \frac{1}{2} C_{nm}\varepsilon_n\varepsilon_m
\tag{2.27}
$$

Now, subtracting equation (2.27) from equation (2.25) we get

$$
C_{mn} = C_{nm}
\tag{2.28}
$$

Thus stiffness is symmetric and has 21 independent elastic constants. These 21 independent elastic constants can further be reduced by considering the symmetry conditions found in different crystals.

In particular for a cubic lattice due to higher symmetry there are only three independent elastic constants C_{11}, C_{12} and C_{44}.

$$\text{i.e. } C_{cubic} = \begin{pmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{pmatrix} \qquad (2.29)$$

Explicit form of other lattice symmetries can be found in ref [79].

In principle there are two ways of calculating the elastic constants of a material from the ab initio methods, the stress theorem [76] and the energy approach [77]. The stress theorem relies on the ab initio approach to directly calculate the stress tensor. And once the stress tensor has been computed by ab initio method, the elastic constants are directly derived from the generalised Hook's law in equation (2.18). In our calculations of elastic constant we have used the energy approach. The energy approach is based on the computed total energy of properly selected strained states of crystal and is given in detail in Chapter 3, Computational Tools.