Chapter 1

Introduction

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1.1 Introduction

Thirty years ago, it was forecasted that our modern society would be supported and operated mainly by three elements of technology which are materials, energy and information. Today, that prediction seems to be more and more realized. Especially, the rapid rise in the research and development of new materials has not only largely improved our modern life but also controls further expansions of other two technologies. As a result, during last three decades, there has been a continuous progress in the study of various physical and chemical properties of elemental solids, their compounds and alloys. The main reason behind the increased study is that these compounds and alloys have found large number of applications in the field of material science and industries [1]. The limitations of elemental solids, due to their limited physiochemical properties could be overcome by alloys and compounds formed of such elemental solids. Alloys composed of metals and non metals as well as those composed of metals only are found to have exceptional physical and chemical properties. For example, aluminium based intermetallic alloys are found to have low mass, high strength, high oxidation resistance etc. which make them useful in many industrial applications [2]. Carbides composed of metal-carbon as well as semiconductor-carbon like Zirconium Carbide (ZrC) and Silicon carbide (SiC) are also of technologically important materials. ZrC is an attractive material in nuclear industry and it has unique physical properties like high hardness and high melting temperature [3]. On the other hand, SiC is a material with large hugoniot elastic limit (HEL) [4]. It has found large number of applications in high pressure research and it is considered as a suitable candidate for replacing diamond. Alkali halides, in particular alkali fluorides like Lithium Flouride (LiF) and Sodium Flouride (NaF) show exceptional physical properties under high pressure conditions with chemical inertness. As a result, they have found applications as a pressure transmitting medium [5]. Metal-oxides are also a subject of great interest. In particular, alkaline earth oxides are important constituents of earth’s lower mantle, where pressure reaches up to 140 GPa [6]. As a result, they are of great geophysical interest. The relative stability of different crystallographic phases and possible high pressure phase transformations among these oxides has been a long standing interest. Despite of their extensive studies, some interesting problems remains unresolved and a number of basic properties are still unknown.
Binary and bulk metallic glasses [7] as well as liquid metals and their alloys [8] are also a subject of great interest. Metallic glasses have found large number of important industrial applications. Since, 1990s, the bulk metallic glasses have emerged as a promising class of engineering materials due to their superior physical and mechanical properties originating from the amorphous nature of the structure [9,10].

The fundamental task in the research in this field of science is the development of various experimental and/or theoretical tools. There has been a continuous progress in the experimental and theoretical study of materials. The refined high pressure experiments have made it possible to study response of various materials under high pressure [11]. In situ X-ray [12] and neutron diffraction [13] experiments have been one of the most successful tools in the experimental research for the characterization of materials under normal as well as high pressure and temperature [14]. For the study of liquid metals and their alloys, experimentally, in recent years, combination of container less techniques with synchrotron sources has enabled structural investigations of metallic liquids above the melting point and in supercooled state. Among these techniques, aerodynamic and electromagnetic levitation methods play an important role [15]. Thus, from experimental point of view, there exist several methods for the study of materials in their ground state as well as in extreme conditions like high temperature and/or pressure.

Theoretically also, there are many methods for the study of materials at ambient conditions. In earlier works, most of the calculations of various ground state properties of solids were performed using empirical pseudopotential theories [16]. This theory was found to be quite successful and computationally easy. Using this theory, Soma et al [17, 18] have calculated physical properties of various classes of materials like metals, alloys and compounds in solid phase. The main drawback of this theory is that it involves large number of parameters, the choice of which is made by fitting the calculated physical properties with the corresponding experimental results. Thus, it is obvious that for the empirical theories to be successful, one needs a reliable experimental data either as input or for the fitting procedure. Similarly, model potential formalism is also another way of calculating structural properties of solids and liquids. The first form of the model potential incorporating ion-electron interaction was proposed by Ashcroft [19]. This form of model potential (also known as empty core model) was used to remove the singularities in the wave function.
within the core region. This potential was used by many researchers to calculate various physical properties of metals, alloys and compounds [20-22]. Ashcroft empty core model potential was local in nature, i.e. it depends on the ionic position, only. Following this fact, Hein and Abarenkov [23] have proposed a local model potential with non local effects included. Harrison et al [24] has proposed a point ion model potential, which takes a point ion coulomb potential plus a repulsive exponential function, which tends to cancel the coulomb potential within the core. Shaw et al [25] have proposed the constant core model potential. Several other forms of the model potentials were also proposed by other researchers by including various terms inside and outside the core [26-35]. This model potential formalism including weak ion-electron interaction includes at least one parameter, namely the core radius. The determination of the core radius plays an important role in the calculation of various physical properties. There are many methods proposed for the determination of core radius. One way of calculating the core radius is to find out the value of reciprocal lattice vector at which the screened form factor becomes zero first time [36]. This formula gave very good results of various physical properties of alkali metals and their alloys. However, for transition and noble metals, this approach does not give good results. Hein and Weare [16] have proposed an empirical formula for the determination of core radius of transition metals. This formula only involves the Wigner-Seitz radius of transition metal at given temperature in order to calculate the core radius. This approach is found to be successful for transition metals. Thus, it was observed that model potential formalism is able to predict several properties of metals and alloys with out any fitting procedure. However, there remains another issue regarding the calculation, which is the density at given temperature, which must be used from the experimental data. Thus, there always remains some issue regarding the use of model potential formalism. However, for the liquid phase, where complete ab initio calculations are still scanty, model potential formalism mimics well the structural, vibrational and thermodynamic properties of liquids.

Another way of calculating ground state properties of solids, was opened up by the pioneer work of Hohenberg and Kohn [38] and Kohn and Sham [39], who gave the density functional theory. According to this theory, total energy of many electron system in an external potential is a unique functional of the electron density and that this functional has its minimum at ground state density. Expressing the electron density as a sum over one-electron densities and using the one-electron wave
functions as the variational parameters, we are lead to the Kohn-Sham one-electron equations. With different basis sets, density functional theory is implemented in various first principles codes in different way [40-44]. For instance, in the Full Potential Linear Muffin-Tin Orbital Method (FP-LMTO) [40], in the wave function expansion, linear muffin-tin orbitals are used. The wave function is represented as an expansion of the basis function, usually Bloch functions. The charge density is calculated exactly inside the non-overlapping muffin-tin (MT) or atomic spheres. In the interstitial region, where the charge density is slowly varying, it is represented by a linear combination of Hankel or/and Neumann functions (depending on the sign of the kinetic energy) together with Bessel’s functions fitted to the same values and slopes on all MT spheres. Thus, a basis function in interstitial region is therefore expressed as a Bloch sum of Hankel or/and Neumann functions, which in turn is represented as a Fourier series. Inside the MT spheres, where the charge density varies rapidly, the basis functions are Bloch functions built up of radial functions times spherical harmonics. The radial part of a basis function is constructed by solving the radial Schrödinger equation in a spherical potential at the fixed energy and their energy derivatives for each angular quantum number. The expression for the crystal wave functions in the MT spheres are matched to the interstitial crystal wave function at the sphere boundaries so that the total crystal wave function becomes continuous and differentiable in all space. The potential used to solve Schrödinger equation is obtained from the charge density by solving the Poisson’s equation.

In Full Potential Lineralized Augmented Plane Wave (FP-LAPW) method [41], like FP-LMTO ones, the unit cell is partitioned into overlapping atomic or MT spheres centred around the atomic site, and an interstitial region. For the construction of the basis functions the muffin-tin approximation (MTA) is used according to which the potential is assumed to be spherically symmetric within the atomic spheres but constant outside. The difference between FP-LAPW and FP-LMTO methods lies in the fact that the FP-LAPW method uses atomic like functions within the MT spheres, while the latter employs the Bloch functions built up of radial functions times spherical harmonics. In the interstitial regions FP-LAPW method rather employs plane waves. In this method each plane wave is augmented by a corresponding atomic solution inside each MT spheres. A linearization of the energy dependence of these atomic radial functions is used by solving the radial Schrödinger equation for fixed linearization energy but adding an energy derivative of this function. The
corresponding two coefficients, then, can be chosen so as to match (at the MT sphere boundary) the atomic solution to each plane wave, in value and slope, which determine the two coefficients of the function and its derivative. Latest modification to this method is the use of APW plus (with) local orbitals (APW+lo), where matching is only done in value while keeping the accuracy of LAPW, to give significant computational speed compare to FP-LAPW approach.

In Linear Combination of Atomic Orbitals (LCAO) calculations [42], atomic orbitals are expressed as products of angular momentum eigen functions and radial orbitals, in calculations with periodic boundary conditions appropriate phase factors are added to form correct Bloch functions. The radial functions are either represented numerically or, to facilitate the calculation of multi-centre integrals, in terms of linear combinations of Slater type or Gaussian-type orbitals (STOs and GTOs). In a minimal basis, only LCAOs corresponding to the quantum numbers of the occupied states are used. If orbitals are added which are unoccupied in the electronic ground state, these are called polarization functions. LCAOs are efficient for systems with localized electrons; they are the basis of choice for performing Hartree-Fock calculations [43] and have recently enjoyed renewed popularity.

Plane-wave basis sets [44,45] offer several advantages: (i) Convergences with respect to the completeness of the basis set is easily checked by extending the cut-off energy (i.e. the highest kinetic energy in the PW basis); (ii) Fast-Fourier-transforms facilitate the solution of the Poisson equation; and (iii) Force on the atoms and stresses on the unit cell may be calculated directly via the Hellmann-Feynman theorem, without applying pulay corrections for the site-dependence of the basis set [46]. The drawback is that in order to achieve convergence with a manageable size of the basis set, the strong electron-ion interaction must be replaced by a sufficiently weak pseudopotential. The basic idea of the pseudopotential approach is to project the Schrödinger equation for the valance electrons on to the subspace orthogonal to the core orbitals, eliminating the nodal structure of the valance orbitals close to the core without modifying them in the region where chemical bonding occurs. Much effort has been spent in constructing pseudopotential designed to satisfy the conflicting requirements of accuracy, transferability and computational efficiency. For the s-p bonded main group elements, a variety of pseudo potentials that work well, have been proposed, but the difficult cases are the first-row elements and the transition and rare-earth elements with node-less 2p, 3d and 4f orbitals, where the usual concepts fail.
For these elements the so called ultra-soft pseudo potentials (US-PP) supplementing a PW representation of the smooth part of wave functions, charge densities and potentials with localized augmentation functions are by far the most efficient solution.

One of the main advantages using a plane wave basis set is that its accuracy can be easily controlled. This is related to the fact that, when using such a basis set, we are making no assumptions about the final shape of the orbitals, other than that there is some scale below which they become smoothly varying. However, this also leads to a major disadvantage of using a plane wave basis set, which is that the size of the basis set required for a given system is often far larger than would be required with a localized basis set. This is because, in condensed matter systems, the orbitals tend to oscillate very rapidly in the vicinity of atomic nuclei, and are much more smoothly varying elsewhere. In order to describe this rapid oscillation we must set very large cut-off energy, so that plane waves can be included with very short wavelengths. But, since most of the space in the cell does not contain rapidly oscillating orbitals, most of the computational expense associated with all these plane waves effectively goes to waste. A localized basis set can be tailored such that the basis functions themselves are rapidly oscillating in the vicinity of atomic nuclei and more smoothly oscillating elsewhere, so that the total number of basis functions required for the system is far smaller. The use of pseudopotentials, in conjunction with plane waves, can dramatically reduce the magnitude of this problem. To understand what pseudo potentials do, we note the following important facts about orbitals in condensed matter systems.

The use of pseudopotentials rely on the fact that the core electrons are tightly bound to their host nuclei, and only the valance electrons are involved in chemical bonding. Therefore it is possible to incorporate the core states into a bulk nuclear potential, or pseudopotential, and only deal with the valence electrons separately. Core wave functions are rapidly varying with many nodes, and require a large number of fitting functions to model accurately. Pseudopotentials overcome this as the pseudo-wave function is smoothly varying and node-less within a certain core radius. In addition the columbic interaction of core states would tend to swamp any total energy calculations trying to compare small differences in valance bond energies. In order to remain orthogonal to the core states, the valance states are also forced to become rapidly oscillating near the atomic core, requiring large numbers of fitting functions to model accurately. Pseudopotentials overcome all of these problems. They
become particularly important for the heavier elements when the number of core electrons vastly outweighs the valence electrons. Finally for heavier atoms, in which relativistic effects are important, and so the Dirac equation is required, the valance electrons can be treated non-relativistically. Therefore, removal of the core electrons allows a non-relativistic approach to be maintained.

Thus, in the present work, we have used plane wave pseudopotential density functional theory as implemented in the Quantum ESPRESSO code [44] for the calculation of various ground state properties of solids. The lattice mechanical properties namely phonon dispersion and phonon density of states (p-dos) are calculated using density functional perturbation theory.

Once, the ground state properties are obtained, thermodynamic properties at elevated temperatures and pressures can be obtained using either (i) harmonic approximation or (ii) quasi harmonic approximation or (iii) quasi harmonic Debye model or (iv) mean field potential approach or (v) molecular dynamics simulations.

In harmonic approximation [47], explicit effect of temperature on the structural and lattice mechanical properties are not included. As a result, it fails in explaining properties like temperature dependence of volume, of the elastic constants and phonon frequencies. Also, at high temperatures ($T > \theta_D$), harmonic model has certain limitations.

On the other hand, in quasi harmonic approximation (QHA) [46], effect of temperature on the structural and lattice mechanical properties of solids is included via volume dependence. Further, this approach requires the calculation of phonon frequencies and p-dos at several values of lattice constants around equilibrium, which is quite demanding computationally.

Mean field potential approach proposed by Wang and co workers [47] and further utilized by Bhatt et al [50] is also used for the calculation of thermodynamic properties of solids at elevated temperatures and pressures. This approach calculates the thermodynamic properties in terms of mean potential experienced by ions around equilibrium. One drawback of this approach is that, in evaluation of mean field potential, we need to choose a parameter, $\lambda$, which has three integer values -1, 0 and +1 corresponding to three expressions for the Grüneisen parameter given by Slater [51], Dugdale and Mcdonald [52] and that for free volume theory [53], respectively. Thermal expansion is very much affected by these three different choices of $\lambda$. 
Recently, Bhattacharya et al [54] and Bhatt et al [55] have proposed that $\lambda$ should be used as a fitting parameter to the thermal expansion. Thus, it is observed that the mean field potential does not evaluate thermodynamic properties in a unique way for all class of materials.

Molecular dynamics (MD) simulations [56] and Thermodynamic integration methods [57] are also one of the strong methods for the calculation of thermodynamic properties. MD simulation requires very large size of cell and large number of atoms to be placed in it; as a result, it is computationally expensive. On the other hand, the thermodynamic integration method, which allows the free energy associated with the accurate ground state energy (usually obtained by ab initio calculations) to be related to that of a reference system described by a simple energy function. The key idea is that the difference of free energy in these two systems is considered to be the reversible work done on switching the energy function isothermally from reference to the actual ones. In order to achieve this, one needs a continuously varying energy function, which depends on a “switching parameter”. Then the difference in free energy caused by the infinitesimal change in switching parameter is calculated by the thermal average, which is calculated in the canonical ensemble. The ensemble averaged-free energy difference is then calculated numerically by ab initio MD. Even though, the method is found to be highly successful, it has a couple of limitations. The success or failure of this whole scheme depends heavily on the choice of the reference system because this determines the effort needed to compute the difference in free energy. Since no general prescription can be given for choosing reference system, more or less, the problem steams around choosing a proper reference system so as to ensure thermal fluctuation in free energy difference to be as small as possible. Secondly, the scheme assumes that change in energy function, relating the actual system to the reference system, with respect to switching parameter commutes with the kinetic energy, which prohibits the quantum effects to be included properly, except for a case when the chosen reference system itself includes these effects inherently.

The quasi harmonic Debye model [58] is a simple and accurate method of calculating thermodynamic properties of solids at finite temperatures and/or pressure. It requires as input the cohesive energy and the Poisson’s ratio of the system. Once, the two inputs are obtained using any reliable method, thermodynamic properties can
be calculated in a straightforward way. In the present thesis, thermodynamic properties of solids are calculated using quasi harmonic Debye model.

Like in solid phase, materials that are non crystalline (glassy) and liquid (near and above melting point) are also a class of technologically important. As is known that density functional theory is accurate at ambient conditions, for glassy and liquid materials, it can not be used directly. Orbital free ab initio molecular dynamics simulation (OF-AIMD) [58] and molecular dynamics simulation [60] are the methods to be used at such thermodynamic states of materials. However, due to large computational cost, both the methods are not frequently used.

Embedded atom method (EAM) [61] and Modified Embedded atom method (MEAM) [62] can also be used. The drawback of using EAM and MEAM methods is that it requires the fitting of five to six parameters with the experimental quantities like phonon frequencies, elastic constants etc.

On the other hand, model potential formalism, which uses a model potential to include the weak ion-electron interaction acts as a good substitute for other methods. In this method, structural, lattice mechanical, electrical transport and dynamical properties of liquids and glasses of interest are calculated using a model potential in conjunction with the established theoretical approaches. The only input that this approach requires is the density of materials at desired thermodynamic state. Once, the density is obtained, structural, lattice mechanical, electrical transport and dynamical properties can be calculated quite easily.

In the present study, we have calculated phonon dispersion relation and related elastic constants of metallic glasses (binary and bulk) as well as liquid metals and their alloys using model potential formalism in conjunction with the phenomenological model of Hubbard and Beeby (HB) [63]. Further, electrical transport properties like electrical resistivity, thermoelectric power and thermal conductivity of liquid metals and their alloys are calculated using Ziman theory [64] and Faber-Ziman theory [65]. Dynamical properties like velocity autocorrelation function (VACF) and power spectrum are calculated using theory given by Glass and Rice [66]. More details about the theoretical formulations used in the present work are given in detail in the next chapters.
The properties studied in detail in the present work are,

- Total energy of solids at ambient condition
- Phonon dispersion along major symmetry directions at zero and high pressures
- Phonon density of states (p-dos) at zero and high pressures
- Pressure induced structural phase transition
- Thermal expansion
- Static equation of state (p-v relation)
- Temperature variation of free energy
- Quasi harmonic phonon dispersion and corresponding p-dos at elevated temperatures
- Temperature variation of isothermal and adiabatic bulk modulus
- Temperature variation of thermodynamic Grüneisen parameter
- Temperature variation of Debye temperature
- Pressure variation of Debye temperature
- Temperature variation of specific heats
- Melting curve of materials
- Phonon dispersion relation and related elastic properties of metallic glasses as well as liquid metals and their alloys
- Electrical transport properties of liquid metals and their alloys
- Dynamical properties of liquid metals and their alloys
1.2 Chapterization

The thesis is planned as following.

The first chapter deals with the introduction and the general outline of the thesis.

The next chapter 2, describes the theoretical methods used in the present study to calculate various physical properties of materials at ambient conditions and at high pressure using density functional theory as implemented in Quantum ESPRESSO code [44]. Further, we also demonstrate the use of density functional perturbation theory to compute the phonon dispersion along high symmetry directions using density functional perturbation theory. The method to calculate phase transition pressure by calculating the total enthalpies is also shown in this chapter.

Chapter 3 gives the results of ground state and high pressure structural and lattice mechanical properties of solids at 0 K temperature. Further, it also discusses the results of pressure induced structural phase transitions. All the calculations are carried out using density functional theory as implemented in Quantum ESPRESSO code [44]. The computed results are compared with the experimental and other theoretical results available in literature.

The results of finite temperature thermophysical properties of solid materials are described in chapter 4. All the calculations of finite temperature thermophysical properties are carried out using quasi harmonic Debye model [56]. The computed values are compared with the recent experimental and theoretical findings.

Chapter 5 describes the results of high pressure melting curve of materials. The calculation of high pressure melting curve is carried out using Lindemann’s law. In the present work, the important ingredient is the pressure dependent thermodynamic Grüneisen parameter, which is deduced using the quasi harmonic Debye model [56].

Phonon dispersion relation and related elastic properties of binary and bulk metallic glasses are discussed in chapter 6. The calculations of phonon dispersion relation are performed using model potential formalism in conjunction with the Hubbard-Beeby model [61]. From the long wavelength limit of phonon frequencies, various elastic
constants are calculated and are compared with the experimental and other theoretical findings.

The results of collective dynamics of liquid aluminum and its binary liquid alloys are described in chapter 7. All the calculations are carried out using model potential formalism in conjunction with the Hubbard-Beeby model [61]. From the long wavelength limit of the phonon frequencies, various elastic constants are computed and are compared with the available experimental and theoretical findings.

Chapter 8 describes the results of electrical transport properties of liquid metals and binary liquid alloys. The electrical transport properties are calculated using Faber-Ziman model [63]. The computed values are compared with the recent experimental and other theoretical findings.

In chapter 9, we describe the results of dynamical properties of liquid metals and binary liquid alloys. The dynamical properties of melts are computed using model given by Glass and Rice [64]. The computed dynamical properties are discussed in the light of experimental and theoretical findings available in literature.

The conclusion and future scope of the present work are given in chapter 10.
1.3 References


12) A.C. Lawson, D.P. Butt, J.W. Richardson and J. Li, Phil. Mag. 87 (2007) 2507


23) V. Heine and I. Abrankov, Phil. Mag. 9 (1964) 451
27) A.R. Jivani, P.N. Gajjar and A.R. Jani, Semiconductor Physics, Quantum Electronics and Optoelectronics 5 (2002) 243
35) P.N. Gajjar, B.Y. Thakore and A.R. Jani, Solid State Communications (Great Britain) 100 (1996) 785
38) P. Hohenberg and W. Kohn, Phys. Rev. 136 (1964) B864
40) www.ihp-ffo.ed/-msm
45) www.pwscf.org
46) P. Pulay, Molec. Phys. 17 (1969) 197
47) K. Parlinski, Computer code PHONON (Poland: University of Cracow) 2005
52) J.S. Dugdale and D.K.C. Mc Donald, Phys. Rev. 89 (1953) 832
64) J.M. Ziman, Phil. Mag. 6 (1961) 1013
65) T.E. Faber and J.M. Ziman, Phil. Mag. 11 (1965) 153