1.1 Introduction

Materials are always an integral part of human culture and civilization. They exist in four states viz. solid, liquid, gas and plasma. Consequently, their properties depend on their internal structure, which influences their performance in different conditions. From the macroscopic point of view, the existence of substances in different phases is generally related to (i) temperature (ii) pressure and (iii) volume. It is a fact that the solid state of matter exists at low temperature and volume, the gaseous when the temperature and volume are very high and the liquid state when the temperature and volume have their intermediate values. The plasma state occurs at extreme high pressure and temperature conditions. Microscopically their existence depends on their internal structure [1.1].

A very big advancement in the studies of these states of matter had occurred in the last century and the branch of physics dealing with this study which has emerged out is known as “condensed matter physics”. It mainly concerns with the macroscopic physical properties of matter, and particularly deals with the condensed phases which appear whenever the number of constituents in a system is extremely large and so that the interactions among the constituents are very strong. It has a large overlap with statistical physics, chemistry, materials science, fluid and solid mechanics, nanotechnology and engineering. These involve different types of research on thousands of different materials, in both pure and applied fields.

This science of condensed phase of matter begins with the crystal, its single most important structural idea. The two broad sub-areas of solids and liquids are paid much attention in this regard. Solids can be broadly classified as either crystalline or amorphous (non-crystalline) phase. The crystalline phases are characterized by ordered or regular arrangements of their basis (ions, atoms or molecules). The arrangement of atoms in crystalline materials is responsible for most of their characteristics. By knowing the arrangement of atoms in a unit cell of a crystal, the entire structure may be described by repeating process in a periodic manner. But this is not true for the amorphous materials because of their disordered or irregular structure. An amorphous solid is a solid in which there is no long-range order of the positions of the atoms. A perfect crystal is a completely ordered material while a deviation in structure and
properties creates the disorderliness. A material at absolute temperature may be considered as highly ordered system while rise in temperature, pressure and volume creates disordered states. Also an impurity in a pure material develops defects in their structure and thus develops disorderliness. Glasses, alloys, liquid crystals, plasmas, gels, dense gasses and super-fluids etc. are disordered materials [1.2-1.6].

Comparative to solid the liquid form of matter does not have permanent structure, and also due to unavailability of ideal structure concept as in solids and gas states, the liquid state theory is moderately hard to formulate. One of the important characteristics of liquid is its isotropicness in nature which arises from the time-averaged motion of the constituent ions, atoms or molecules. In liquid state the long range order of the solid has been greatly decreased but the complete thermal disorder of the gas has not been acquired [1.7]. The short range order character develops when solid converts into a liquid. This interesting characteristic of liquid makes it more prominent candidate in metallurgical applications. There are many conceptual models for the example; it is argued that a liquid is similar to the dense fluid of hard sphere in thermal equilibrium with its container. If this or any other simple approximation applies, it should be expected that liquid properties should show systematic trends and relationships [1.8].

The advent of binary mixtures has been one of the most exciting events in the field of materials science and engineering, and such studies are contributing immensely in the field of condensed matter and materials sciences. The characteristic behavior of alloys generates manifold interests for experimentalists as well as theoreticians. Largely, by trial and error, and over a period of many years, it has been found that the properties of many metals (Solid or liquid) and their binary alloys can be significantly improved and their usefulness correspondingly has increased by the addition of more components, which give rise to multi component alloy systems. The development of new materials is traditionally a very tedious process involving extensive experimental and theoretical investigations by which composition and processing conditions are varied in a more or less erratic manner until the desired properties are achieved. The properties of these alloys depend on their composition and how these are geometrically arranged [1.9]. Therefore, detailed information about temperature and composition, range of stability on a desired phase are indispensable for a full understanding of the properties and possible applications of a given material. This becomes true for metallic complexes and ceramic alloys as well as for binary combination of alloys.
The scientific research activities are broadly classified as experimental and theoretical research. The experiments are direct way to establish relationships in nature. Two elements of the experiment are equipment and operation, which impose some restrictions on the activities. Experimental equipment may exhaust a lot monetary resources, and operation needs human beings to face expensive or potentially unachievable conditions and exposure to dangerous materials. This leads to the fact that some hypotheses can not be tested directly experimentally. In such cases computational simulations can be an inexpensive and safe replacement. With relevant theoretical models, one can get results from computational simulations which are comparable to the experiments which makes a valuable complement to experiment and push the development of science.

Virtually all of the properties of metals are determined by the valence electrons. Most of the calculations of the physical properties of a metal require the knowledge of the band electrons and interactions among the ion cores. The total lattice potential could be calculated in principle, by solving the Schrödinger equation for a system of interacting nuclei and electrons that form the crystal. Thus, this is a many body problem and is difficult to solve exactly. Hence it requires some unavoidable approximations like adiabatic or one-electron approximation.

In the last century, along with the development of computers, many computational methods were developed for various fields of science. In computational chemistry, among these methods, methods based on quantum mechanics i.e. pseudopotential and density functional theory (DFT) are well accepted and admired methods [1.10-1.11]. The concept of pseudopotential, which has been developed within the one-electron model over the past four decades, appears at first sight artificial and inconsistent. But the method of pseudopotential with its relative computational simplicity and capability of predicting most of the properties of perfect and imperfect crystals, alloys, liquids, amorphous materials and metallic glasses with and without external influences, is considered one of the most important theory in the field of solid state physics.

It is noted that interaction potential between ion and electron with its Coulomb singularity at the nucleus may be replaced by a non-singular potential called "pseudopotential". This replacement is such that the electron do not notice much change for a given system each leading to essentially the same overall picture. This
method is actually designed to overcome the limitation of plane wave method in calculation of band structure of materials [1.12].

The pseudopotential theory provides insight into virtually every aspects of the behaviour of electrons in a system. Today, knowledge of pseudism is mandatory for anyone interested in a thorough understanding of properties of condensed matter.

The term pseudopotential is defined as [1.13]:

"The fictitious weak and effective potential experienced by an electron in the vicinity of the ions and clouds of surrounding electrons".

In brief, we can say that in pseudopotential theory, model potential is constructed or formulated in such a way that the energy eigenvalue turns out to be same as that in the case of exact wave equation. This weak potential is generally non-local in character (depends on energy and position). Though sometimes for the simplification of computations it is replaced by local model potential (depends on position only).

With the enhancement in main-frame computers nowadays, the Density functional theory (DFT) is also emerging as a successful tool in determining various solid state properties of materials. These approaches are basically starting point to study the electronic structure of matter and it leads to predict various physical, chemical, electronic, electric, optical and magnetic properties of matter.

DFT is an extremely successful approach for the description of ground state properties of metals, semiconductors, and insulators. The success of DFT not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes [1.14]. The main idea of DFT is to describe an interacting system of fermions via its density and not via its many-body wave function. For N electrons in a solid, which obey the Pauli’s principle and repulse each other via the Coulomb potential, this means that the basic variable of the system depends only on three the spatial coordinates x, y, and z rather than 3N degrees of freedom.

DFT has its conceptual roots in the Thomas-Fermi model, DFT was put on a firm theoretical footing by the two Hohenberg-Kohn theorems (HK) [1.15-1.16]. The original HK theorems held only for non-degenerate ground states in the absence of a magnetic
The first HK theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates. It lays the groundwork for reducing the many-body problem of N electrons with 3N spatial coordinates to only 3 spatial coordinates, through the use of functionals of the electron density [1.17].

The second H-K theorem defines energy functional for the system and proves that the correct ground state electron density minimizes this energy functional. Within the framework of Kohn-Sham DFT, the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the exchange and correlation interactions. Modeling the latter two interactions becomes the difficulty within KS DFT. The simplest approximation is the local-density approximation (LDA) [1.18], which is based upon exact exchange energy for a uniform electron gas, which can be obtained from the Thomas-Fermi model, and from fits to the correlation energy for a uniform electron gas. Non-interacting systems are relatively easy to solve as the wave function can be represented as a Slater determinant of orbitals. Further, the kinetic energy functional of such a system is known exactly. The exchange-correlation part of the total-energy functional remains unknown and must be approximated.

While DFT in principle gives a good description of ground state properties, practical applications of DFT are based on only one approximation, the so-called exchange-correlation potential. The exchange-correlation potential describes the effects of the Pauli principle and the Coulomb potential beyond a pure electrostatic interaction of the electrons. Possessing the exact exchange-correlation potential means that we solved the many-body problem exactly, this is clearly not feasible in solids. Answer to this is the common approximation known as local density approximation (LDA) which locally substitutes the exchange-correlation energy density of an inhomogeneous system by that of an electron gas evaluated at the local density.

While many ground state properties (lattice constants, bulk moduli, etc.) are well described in the LDA, few other properties (dielectric constant) are overestimated by 10-40 % in LDA compared to experiment. This overestimation stems from the neglect
of a polarization-dependent exchange correlation field in LDA. To overcome this difficulties new approximation known as generalized gradient approximations (GGA) [1.19-1.20] is emerging out nowadays, through which good prediction of the properties at ground state and at other ambient conditions are possible. The details regarding DFT and exchange potential and the approximations are discussed briefly in the coming chapters.

It has been noticed from the literature survey that the concept of pseudopotential is well established in the theory of condensed matter, which helps us in understanding various properties including physical as well as chemical properties of crystalline and amorphous materials [1.21-1.22]. The concept is emerged as direct consequences of quantum mechanical scattering theory. The theoretical computational scheme, pseudopotential provides an efficient representation of the external potential for the valence electrons in metallic systems. It actually provides insight into virtually every aspects of the behaviour of electrons in a system of condensed matter. It should be noted that, the comprehensive unified studies of several metals with pseudopotential method have generated very good results and at the same time comprehensive study of solid metals, alloys, liquid metals their binary and multi component systems using pseudopotential is rare. This aspect motivated us to investigate the structural, vibrational, electronic, and elastic properties of materials in all their different phases. The pseudopotential concept is particularly valuable because of its relevant computational simplicity and capability of predictions almost all the properties of perfect and imperfect crystals, alloys and liquids, amorphous substances and metallic glasses with or without external influences.

The method of pseudopotentials is simple conceptually. The results properly generated by this method are well comparable with those obtained from the first principle-all electron calculation. With certain approximation, fairly reliable analytical forms of interatomic interactions can be obtained. Via perturbation expansion, it directly provides the information of many body forces in metals. It is interesting to note here that, in spite of of impressive success of pseudopotential theory in solving specific problems attempts of comprehensive studies to metallic complexes are surprisingly rare, even with a local pseudopotential and it still remains a problem of interest. The electronic structure calculations, especially those using density-functional theory have provided much insight into various properties of different materials in the recent decades [1.23]. However, the computational complexity associated with electronic
structure calculations has restricted these investigations to periodic geometries with small cell-sizes (computational domains) consisting of few hundred atoms (about 200 atoms). But material properties are influenced by defects-vacancies, dopants, dislocations, cracks, free surfaces in small concentrations (parts per million) etc. A complete description of such defects must include both the electronic structure of the core at the fine (sub-nanometer) scale and also elastic and electrostatic interactions at the coarse (micrometer and beyond) scale. This in turn requires electronic structure calculations at macroscopic scales, involving millions of atoms, well beyond the current capability. The present thesis would give the glimpse to the development of a seamless multi-scale scheme, of density-functional and pseudopotential theory to address the general material as a significant issue, thus, paving the way to an accurate structural, electronic, elastic and vibrational study of materials in general.

Looking to the simplicity and various advantages of the pseudopotential and density functional theory, the main aim of the present thesis entitled "PHYSICAL PROPERTIES OF SEVERAL ELEMENTS, COMPOUNDS AND ALLOYS USING PSEUDOPOTENTIALS AND DENSITY FUNCTIONAL THEORY" is to carry out the theoretical investigation of the structural, electronic, vibrational and elastic properties of solid metals and compounds, structural investigation of liquid metals and their binary and multi-component alloys, electronic transport properties and vibrational dynamics as well as superconducting state properties of glass materials. Hence this present thesis will serve to be a good literature based on pseudopotential and DFT calculations/predictions for general matter in all the respect, and can be a bridge between experiments and theoretical prediction about general properties of matter.

The present work reported in this thesis is carried out with the following objectives:

- To study structural, electronic, elastic and vibrational properties of materials, at ground state.
- To predict the possible high pressure phase transitions and transition pressure in solids.
- To generate accurate equation of state of metals and alloys.
- To validate the applicability and efficiency of density functional theory in predicting ground state properties of matter in diverse phases.
- To study application of well characterized model potential for explaining the electron-ion interaction in the liquid metals, binary liquid alloys and multi-component liquid alloys.
Chapter 1

❖ To explore different methods to calculate liquid structure factor and pair correlations for simple, non-simple metals and their binary compounds.
❖ To investigate the electronic transport properties of liquid metals, their binary components.
❖ To study the vibrational dynamics in non-crystalline solids/glasses and hence elastic properties of same.
❖ To predict the superconducting state parameter of various glasses.
❖ To check the impact of various local field correlation functions in a model potential to judge the screening influences.
❖ To infer the effect of the concentration (x) on the electronic properties in the A_{1-x}B_{x} alloy.

To have a qualitative and quantitative picture as well as to draw final conclusions out of a research problem, the proper presentation of the research output plays an important role. Hence in the present study, the content of the thesis has been organized into various chapters. The overview of all the chapters is as follows:

This present Chapter 1, in general gives brief introduction of the pseudopotential theory and shows its capabilities as a tool for calculating and understanding various properties of matter. This also gives an overview of the whole thesis including some important literature survey based on the density functional approach using plane wave pseudopotential method and use of model pseudopotentials relevant to present study.

The next Chapter 2, describes the introductory part of pseudopotential theory. The nature of model potential based on sound physical ground is presented and the role of screening and various forms of local field correlation functions considered in present study is mentioned elaborately. And thus model potential approach is discussed in details in this chapter. The detailed unscreened, screened and form factor of the model potentials and the determination of the parameter of the model potential [1.24] are also presented. The analytical work regarding the computations using the model potential is completed minutely there. In the same chapter the basic concept of plane wave density functional theory (DFT) is discussed and the general flow (flowchart) of density functional program relevant to the present study is also narrated in concise. The only
approximations in DFT i.e. LDA and GGA as exchange and correlation are also confer in
details followed by general theory of DFT.

In the **Chapter 3** of present thesis the outcome of the calculations of properties
like band structure, equilibrium lattice parameter, bulk modulus, pressure derivatives,
equation of state (Pressure – Volume relations), possible high pressure phase
transitions, density of state, elastic constants, vibrational properties like phonons and
phonon density of state for metals and alloys in solids phase are narrated in detail. The
shape of crystal structure and charge density plot along Miller plane for few alloys are
also discussed along with first Brillouin zones. To make the present thesis more
appealing we have selected good combination of simple and binary solids and try to
cover the broad range of solid materials like Simple Metals, Carbides, Hydrides, Oxides,
Nitrides, Fluorides, Phosphates, Pervoskites, Chalcogenides and few other combination
of alloys.

The Newtonian dynamics to determine liquid structure factor and pair
correlation function using molecular dynamics (MD) [1.25] and *ab-initio* molecular
dynamics (AIMD) [1.26] is described in petite in **Chapter 4.** The AIMD method is than
extended to generate equation of state for aluminum [1.27] with wide-ranging densities
that are useful in characterizing the plasma state as well other explosive phenomenon
[1.28-1.29].

The three methods (PY (Percus-Yevick), CHS(Charged hard sphere)[1.30-1.31]
and OCP(One component plasma) [1.32-1.33]) to generate structure factor for liquid
metals are briefly discussed in first part of **Chapter 5.** The study of electrical resistivity
for liquid metals with the basic background of Ziman’s formula [1.34] is also discussed
in brief. The shear viscosity (an important property of liquid) is presented based on
charged hard sphere approach for few non-simple metals. In latter part the resistivity of
binary combination of liquid metals is described in details with the calculation of partial
structure factors. The concentration sensitivity of electrical resistivity is also shown
along with temperature for liquid binary alloys.

The pseudopotential based investigations of the vibrational dynamics and elastic
properties of glasses are reported in **Chapter 6.** In the formulation to compute the
phonon dispersion, pair correlation function is either generated or recently reported
experimental pair-correlations is used and detail theory of longitudinal and transverse
vibrational frequencies \[1.35\] calculations are discussed. Using such investigation on binary systems the thermodynamic and elastic properties related to disorder structure is predicted. The superconducting state parameters (SSP) \[1.36\] of binary combination of glassy alloys are estimated in the later half of this chapter. The necessary formulation, detailed investigations and resulting outcome for few binary glass alloys are reported in this chapter.

The final and concluding Chapter 7 summarizes the entire work of the present study along with the important general conclusions. Important discussions regarding the applicability and advantage of the density functional theory and presently formulated pseudopotential are also addressed in this chapter. The scope of further investigations of the work is also pointed out at the end. At last there in the Appendix section of same chapter important results like (a) resistivity of multi-component structure factor using complex formation model (b) Equation of state for Al-Li random alloys using model potential and (c) Exploding foils simulations based on equation-of-state generation through \textit{ab-initio} molecular dynamics are narrated with suitable example for liquids. The necessary results and discussions are made at the appropriate point in every chapter. While giving proper shape to the thesis, however, the necessary discussion and comments/remarks are made at the appropriate point in every chapter in the context of various developments and keeping a view on the current trend in the field of DFT & pseudopotential theory. The scope of further investigations of the work is also narrated in the last chapter.

Important and useful references are listed at the end of each chapter for making it a versatile document for the readers and good documentation.
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