Chapter 2
Theoretical Formulation

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2.1 Density Functional Theory

Density functional theory (DFT) is one of the most popular and successful quantum mechanical approaches to study matter. It owes the versatility due to the generality of its fundamental concepts and the flexibility in implementing them. In spite of this flexibility and generality, it is based on a sound conceptual framework. Furthermore, it is computationally simple nowadays. For these reasons it has become a common tool in first-principles calculations aimed at describing or even predicting properties of molecular and condensed matter systems [1-4]. The description of condensed matter using first-principle techniques starts with the atomic number Z and proceeds to develop a description of the system depending on laws of quantum mechanics. Consequently, such a model is able to look closely at the dependence of particular phenomenon on the atomic number Z, as we know the electronic properties of solids and liquids are results of the behavior of the outer shell of valance and/or conduction electrons [5].

The DFT problem is non-trivial. Over the years, many different methods and approaches have been proposed and used, all with different advantages and limitations. It is somewhat surprising to note that most of the methods and codes in use today trace their roots back decades, albeit with significant improvements and additions. This long time scale reflects the large investment in time required to develop computational programs/codes, and the fact that the underlying physical bases for the approaches have not been superseded. With advances in computational power, it is now possible to tackle problem that were completely out of reach just a few year ago [6].

Although the original papers on DFT provide an overview of the method, many of the improvements incorporated in different publications [1-36] related to theory, applicability and extensions that may have been essential in the calculations needed to address different physical problems. In next section we briefly describe the quantum theory of materials with the special emphasize on DFT.

2.1.1 Basic Theory

The starting point of a quantum theory of material is the Hamiltonian of the many ion, many electron systems. The first step towards a reduction of its complexity is the adiabatic or Born-Oppenheimer approximation. Since the dynamics of the electrons occurs at a time-scale that is much faster than that of much heavier ions, it is
legitimate to assume that irrespective of the instantaneous configuration of the ions, the electrons are at every moment in their ground state. The ionic system is described by an effective Hamiltonian with an effective potential composed of the direct ion-ion interaction and the electronic total energy as a function of the ionic coordinates. In most cases (in fact for all but the lighter atoms) the quantum nature of the ionic dynamics may be neglected and the Schrödinger equation based on the Hamiltonian may be replaced by the classical Newtonian equation of motion. This adiabatic approximation rarely breaks down, although for description of certain phenomena (electronic transport, superconductivity, etc.), the coupling of the ionic and electronic dynamics (electron-phonon coupling) is fundamental. In the adiabatic approximation, the Hamiltonian of the many electron system includes the kinetic energy of \( n \) electrons, their interaction with the external potential of \( N \) ions located at the sites \( R_1 \) and the interaction of the electrons with other electrons.

The solution of the time-independent Schrödinger equation may be attempted at different levels of theory. For applications in the field of materials, two approximations, reducing the many electron problems to an effective one electron form are widely used: Hartree-Fock (HF) theory and Density functional theory (DFT).

The basic approximation of HF theory is to approximate the many electron wave functions by an antisymmetrized product of one-electron wave functions and to determine these by a variational condition applied to the expected value of the Hamiltonian. In the resulting one-electron equations, the pair-wise electron-electron repulsion is replaced by the interaction of the electron with the average electrostatic field created by the charge distribution of all other electrons and an additional exchange term keeping electrons of like spin away from each other to account for the Pauli principle. While exchange is treated exactly in HF theory, correlations arising from short-distance coulomb interactions are neglected [9-10].

On the other hand, the DFT, is based on the famous theorem by Hohenberg and Kohn [11], who demonstrated that the total energy of a many-electron system in an external potential is a unique functional of the electron density and that this functional has its minimum at the 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 leads to the Kohn-Sham one-electron equations [12], where the exchange correlation potential has been expressed as the functional derivative of the exchange-correlation energy. Here the only problem is
that the exact form of exchange-correlation functional is unknown. As a result, the core elements of the DFT are the Hohenberg-Kohn theorem [11] and Kohn-Sham equations [12]. In quantum mechanics, all information about any system can be known if one knows wave function of the system. Here, we will exclusively be concerned with the electronic structure of atoms, molecules and solids. The nuclear degrees of freedom (e.g., the crystal lattice in a solid) appear only in the form of potential $V(r)$ acting on the electrons, so that the wave function depends only on the electronic coordinates. Non-relativistically, this wave function is calculated from Schrödinger’s equation, which for a single electron moving in a potential $V(r)$ reads,

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + V(r)\right)\Psi(r) = E\Psi(r) \quad (2.1)$$

If there is more than one electron (i.e., one has a many-body problem), the Schrödinger equation becomes,

$$\left[\sum_i^{N}\left(-\frac{\hbar^2 \nabla^2_i}{2m} + V(r_i)\right) + \sum_{i<j} U(r_i, r_j)\right]\Psi(r_1, r_2, ..., r_N) = E\Psi(r_1, r_2, ..., r_N) \quad (2.2)$$

Here, $N$ is the number of electrons and $U(r_i, r_j)$ is the electron-electron interaction. For a Columbic system (the only type of system we consider here) one has,

$$\hat{U} = \sum_{i<j} U(r_i, r_j) = \sum_{i<j} \frac{q^2}{|r_i - r_j|} \quad (2.3)$$

Note that this is the same operator for any system of particles interacting via the Coulomb interaction, just as the kinetic energy operator,

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 \quad (2.4)$$

is the same for any non-relativistic system. For an atom, e.g.,...
\[ \hat{V} = \sum_i V(r_i) = \sum_i \frac{Q_q}{|r_i - R_k|} \]  

(2.5)

Here, \( Q_q \) is the nuclear charge and \( R_k \) is the nuclear position. When dealing with a single atom, \( R_k \) is usually taken to be the zero of the coordinate system. For a molecule or a solid one has,

\[ \hat{V} = \sum_{i,k} V(r_i) = \sum_i \frac{Q_{kq}}{|r_i - R_k|} \]  

(2.6)

Here the sum on "\( k \)" extends over all nuclei in the system, each with charge \( Q_k = Z_k e \) and position \( R_k \). It is only the special arrangement of the \( R_k \) (together with the corresponding boundary conditions) that distinguishes, fundamentally, a molecule from a solid. Similarly, it is only through the term \( U \) that the (essentially simple) single-body quantum mechanics of equation (2.1) differs from the extremely complex many-body problem. These properties are built into DFT in a very fundamental way.

### 2.1.2 The Hohenberg-Kohn Theorem

In the Hohenberg-Kohn theorem, the system of \( N \) interacting electrons under an external potential \( V(r) \) (usually the Coulomb potential of the nuclei) is considered. If the system has a non-degenerate ground state, it is obvious that there is only one ground-state charge density \( n(r) \) that corresponds to a given \( V(r) \). In 1964, Hohenberg and Kohn [11] demonstrated that there is only one external potential \( V(r) \) that yields a given ground-state charge density \( n(r) \). The demonstration is very simple and uses a reduction absurdum argument. Let us consider a many-electron Hamiltonian \( H = T + U + V \); with ground-state wave function \( \Psi \). \( T \) is the kinetic energy, \( U \) the electron-electron interaction and \( V \) is the external potential. The charge density \( n(r) \) is defined as,

\[ n(r) = N \int \left| \Psi(r_1, r_2, \ldots, r_N) \right|^2 dr_1 dr_2 \ldots dr_N \]  

(2.7)

Let us consider now a different Hamiltonian \( H' = T + U + V' \) (\( V \) and \( V' \) do not differ simply by a constant: \( V - V' \neq \) constant), with ground state wave function \( \Psi' \).
Let us assume that the ground state charge densities are the same: \( n[V] = n[V'] \). The following inequality holds:

\[
E' = \langle \Psi | H | \Psi' \rangle = \langle \Psi | H | \Psi \rangle = \langle \Psi | H + V' - V | \Psi \rangle
\] (2.8)

That is,

\[
E' < E + \int (V(r) - V'(r)) n(r) dr
\] (2.9)

The inequality is strict because \( \Psi \) and \( \Psi' \) are different, being eigen-states of different Hamiltonians. By reversing the primed and unprimed quantities, one obtains an absurd result. This demonstrates that no two different potentials can have the same charge density. A subtle point about the existence of the potential corresponding to a given ground state charge density, and the various extensions of the Hohenberg and Kohn theorem, are discussed in the specialized literature [11]. A straightforward consequence of the first Hohenberg and Kohn theorem is that the ground state energy \( E \) is also uniquely determined by the ground–state charge density. In mathematical terms \( E \) is a functional \( E[n(r)] \) of \( n(r) \) and hence we can write,

\[
E[n(r)] = \langle \Psi | T + U - V | \Psi' \rangle = \langle \Psi | T + U | \Psi \rangle + \langle \Psi | V | \Psi \rangle
\] 

\[
= F[n(r)] + \int n(r) V(r) dr
\] (2.10)

Here, \( F[n(r)] \) is a universal functional of charge density \( n(r) \) and not \( V(r) \). Furthermore, the minimum value of \( E \) is \( E_o \), the ground state electronic energy. This is an exact result and in principle, means that the ground state energy and electron density may be found using a variational minimization over the electron density, a process which scales linearly with system size. Unfortunately, the proof of the Hohenberg-Kohn theorem is not constructive, hence the form of the functional \( F[n(r)] \) in equation is not known. Kohn and Sham postulated [12] that this functional could be written as,

\[
F[n(r)] = T_e[n(r)] + \frac{e^2}{2} \int \int \frac{n(r)n(r')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + E_{xc}[n(r)]
\] (2.11)
where, the first term \( T_s[n(r)] \) is the kinetic energy of a system of non-interacting electrons with density \( n(r) \) and the second is electron-electron Hartree interaction. The final term, \( E_{xc}[n(r)] \), is the exchange-correlation energy. By writing the electron density in terms of a set of single particle wave functions \( \{\Psi_i\} \) such that,

\[
n(r) = \sum_i |\Psi_i(r)|^2 \tag{2.12}
\]

The kinetic energy term may be written as,

\[
T_s[n(r)] = \sum_i \left( -\frac{\hbar^2}{2m_e} \int \Psi_i^* \nabla \Psi_i r^2 \right) \tag{2.13}
\]

Minimizing \( E[n(r)] \) with respect to \( n(r) \) subject to the constraint that the number of electrons must be constant, lead us to a set of equations for each \( i, \)

\[
\left( \frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}} \right) \Psi_i(r) = E_i \Psi_i(r) \tag{2.14}
\]

,where, \( V_{\text{eff}}(r) \) is an ‘effective potential’ given by,

\[
V_{\text{eff}} = V_{\text{ext}}(r) + \frac{e^2 n(r)}{|r - r'|} d^3 r + V_{\text{xc}}(r) \tag{2.15}
\]

and \( V_{\text{xc}}(r) \) is the exchange-correlation potential \( \frac{\partial E_{xc}}{\partial n(r)} \). \( V_{\text{ext}}(r) \) is the external potential. Equation (2.14) can be seen to be a set of Schrödinger-like equations for the single particle Kohn-Sham orbital,

\[
\hat{H}_{ks} |\Psi_i\rangle = E_i |\Psi_i\rangle \tag{2.16}
\]

Thus, the problem of a system of interacting electrons has been mapped on to a system of non-interacting electrons moving in an effective potential given by
equation (2.16). However, the expression of the density in terms of a set of single particle orbitals has increased the complexity of the problem. The minimization must now be performed over NM degrees of freedom where, M is the number of basis functions used to represent the \( \{\Psi_i\} \).

In practice, numerical solution of the KS differential equation typically proceeds by expanding the KS orbitals in a suitable set of basis functions and solving the resulting secular equation for the coefficients in this expansion and/or for the eigenvalues for which it has a solution [13-17]. The construction of suitable basis functions is a major task within electronic-structure theory (DFT). A basis function set in DFT is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined. Usually these functions are atomic orbitals. Additionally, basis sets composed of sets of plane waves down to a cutoff wavelength are often used, especially in calculations involving systems with periodic boundary conditions.

### 2.1.3 Basis Functions

The wave-functions must be represented as a linear combination of a finite number of basis functions. The choice of the basis determines the achievable accuracy and computational efficiency. In addition, different basis sets may be more or less convenient for calculating given materials properties.

Methods applicable to complex systems employ mostly one of three types of basis sets, namely: (i) linear combinations of atomic orbital (LCAOs); (ii) linearized augmented plane waves (LAPWs); (iii) plane waves (PWs) in combination with pseudopotentials for describing the electron-ion interaction. The choice of a basis is problematic because near to an atom wave functions and potential are atomic-like (i.e. almost spherical-symmetric and strongly varying with radial distance), while in the interstitial regions potential and wave functions are quite smooth.

In LCAO calculations, 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 and have recently enjoyed renewed popularity. [18-20]

In the LAPW approach, space is divided into spheres centered on the atomic sites and the interstitial region. Within the spheres the basis functions are spherical waves, in the interstitial region, plane waves are used. The coefficients of the atomic-like expansion within the spheres and of its energy derivative are chosen such that they match the plane wave expansions at the sphere boundaries in value and slope. The intrinsic energy dependence of the eigen-functions is linearized by expanding the orbitals to first order with respect to the deviation from an appropriately chosen reference energy [21], thus transforming the non-linear into a linear eigen-value problem. Modern versions of the LAPW method do not use any shape approximation to the effective one-electron potential and are therefore referred to as full-potential-LAPW or short FLAPW [22,23]. Similar basis sets are used also in the linear-muffin-tin-orbital (LMTO) [24-26] and Kohn-Korringa-Rostocker (KKR) [27] methods. The LMTO method using the so-called atomic-sphere approximation (ASA) replacing the Wigner-seitz sphere of equal volume is attractive because of its high computational efficiency. A canonical transformation to the most localized LMTO basis allows contact to be made with LCAO-based techniques in the form of the tight-binding LMTO technique [28]. The TB-LMTO method is particularly well suited for performing calculations in real space without using Bloch’s theorem and is hence particularly well suited for periodic systems.

Plane-wave basis sets 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 [29]. 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 pseudo potential. The basic idea of the pseudo potential approach is to project the Schrödinger equation for the valance electrons on to the subspace orthogonal to the core orbitals [30,31], 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 pseudopotentials that work well, have been proposed [32-37], 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 ultrasoft pseudopotentials (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 [37,38].

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 [32-38], 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 valence electrons can be treated non-relativistically. Therefore removal of the core electrons allows a non-relativistic approach to be maintained.

As said earlier, pseudopotentials assume that the localized core states do not take part in bonding, and so can be incorporated as a change in the charge state of the nucleus. Between the nucleus and some cut-off radius $r_c$, the all electron valance wave functions can be replaced with a smoothed form; beyond this radius the pseudo-wave function must be identical to the full all-electron wave function. In addition there will still be exchange interactions between core and valance electrons, which must be included in the potentials. Finally, if self-consistency is to be easily achieved in the calculations then the potentials must have the correct atomic charge density outside the core (norm-conserving pseudopotentials) [37-46].
Figure 2.1 shows the real and pseudo wave function. It can be seen that the rapidly varying core region has been smoothed in the pseudo-wave function but beyond the cut-off radius ($r_c$), the pseudo and all-electron wave-functions are identical.

There are four fundamental properties which these pseudo-potentials display:

1) Real and pseudo-valance eigenvalues agree for a chosen “prototype” atomic configuration.
2) Real and pseudo-atomic wave functions agree beyond $r_c$, the “core radius”.
3) The integrals from 0 to $r$ of the real and pseudo charge densities agree for $r > r_c$ for each valance state (norm conservation).
4) The logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $r > r_c$.

Here, it should be noticed that the last two points are essential if the pseudo potential is to have optimum transferability.
2.1.4 Plane wave pseudopotential method

Orbitals representing electrons that are not core electrons oscillate very rapidly in the vicinity of atomic nuclei, but most of this oscillation can be put down to the fact that they have to be orthogonal to the core electrons.

A pseudopotential essentially changes part of what the outer or valance electrons ‘see’ and hence the core electrons and the potential due to the bare nuclear charge are replaced by a fictitious potential that is defined such that the behavior of the valance electrons is not affected outside some cut off radius from the nucleus. So long as this radius is not so large that it overlaps regions of space that are involved in chemical bonding, the pseudopotential approximation should not significantly alter the inter-atomic interactions that govern the behavior of condensed matter. By using pseudo potentials, the computational cost of a calculation is reduced in four ways [46]:

1. By effectively removing core electrons from the calculation, the number of Kohn-Sham orbitals is reduced. This reduces the memory required to store the orbitals, the time required to evaluate orbital-dependant quantities, and the time required to orthonormalise a set of orbitals.

2. Because there are no core-electrons to which valance electrons must be orthogonal, there is less oscillation of the corresponding orbitals in the vicinity of the nucleus. This means that lower cut-off energy can be used to represent the orbitals, resulting in lower memory requirements and greater speed. This lowering of the cut-off energy is typically a few orders of magnitude resulting in massive gains in efficiency.

3. Because the pseudopotential is not uniquely defined for a particular element, we can optimize the shape of the potential so as to give as low required cut-off energy as possible. Again, this reduces memory and increases speed.

4. Because we only explicitly treat the valance electrons in a calculation when using pseudopotentials, we tend to think of the system as being made of electrons and ions rather than electrons and nuclei.

2.1.5 Exchange-correlation functional

Although, density functional theory is accurate in determining various physical properties of solids at ambient condition, the main limitation of theory is that the exact form of exchange-correlation functional is not known. As a result, some
approximation for this functional has to be used for the calculation. This limitation does not allow the theory to become “exact”. Although, the role of exchange-correlation functional is very minor; it affects the accuracy of any self consistent calculations largely. The widely used two forms of exchange-correlation functional are local density approximation and generalized gradient approximation. Nowadays, hybrid functional is also developed for the further accuracy of calculations.

2.1.5.1 Local Density Approximation

The first practical approximation in DFT is to assume that the exchange-correlation energy of a single electron at the position \( r \) is equal to the exchange-correlation energy of an electron gas of a density \( n_0 \) equal to the local electron density \( n(r) \). A HF description of the electron gas leads to a simple form of the exchange-only energy functional \( E_x[n(r)] \). A much more accurate exchange correlation energy for the homogeneous electron gas as a function of density may be derived from quantum MC simulations [47] and used to construct exchange-correlation functional within the frame-work of a local density approximation (LDA), the most widely used such functional are due to Von Barth and Hedin [48], Perdew and Zunger [49], and Vosko et al. [50]. The relaxation of the constraint of an equal occupation of spin-up and spin-down states and the minimization of the total energy with respect to spin occupancy leads to the local spin density approximation (LSDA), which allows magnetic properties of atoms, molecules and solids to be treated [48]. However, within a non-relativistic or scalar-relativistic description the spin direction is not coupled to the spatial degrees of freedom. Spin-orbit coupling is introduced only through a relativistic description on the basis of the Dirac equation. Alternatively, it may be added to a scalar-relativistic approach as a final perturbation [51].

The LDA is generally very successful in predicting structures and macroscopic properties, but some shortcomings are notorious as well. These concern in particular:

1. Energies of excited states and in particular band gaps in semiconductors and insulators are systematically underestimated. This is after all not so surprising since DFT is based on a theorem referring to the ground state only.
ii. There is a general tendency to over-binding, i.e. cohesive energies are significantly overestimated and lattice parameters are underestimated by up to 3%.

iii. The wrong ground state is predicted for some magnetic systems and for strongly correlated systems.

iv. Van der Waals interactions are not approximately described in the LDA, although there are some recent suggestions for overcoming this problem [52-54].

2.1.5.2 Generalized Gradient Approximations (GGA)

Attributing the limitations of the local description to the neglect of the dependence of the exchange-correlation functional on the local variations of the electron density, generalized gradient approximations (GGA) have been introduced. In the GGA, there is an explicit dependence of the exchange-correlation functional on the gradient of the electron density. As a straightforward expansion in terms of the gradient violates the sum-rules for the exchange hole, generalized gradient expansions corrected for the sum-rules have been proposed by a number of authors. However, at the moment there is as yet no consensus on the best GGA. For solid-state applications, the GGAs Proposed by Predew and co-workers [55, 57-59] have been widely used and have proved to be quite successful in correcting some of the deficiencies of the LDA: the over-binding is largely corrected (i.e. the GGAs lead to large lattice constants and lower cohesive energies) [60, 61] and the correct magnetic ground state is predicted (this also includes a greatly improved prediction of magneto-volume and magneto-structural effects). However, there are also cases where the GGA over-corrects the deficiencies of the LDA and leads to an under-binding. The various exchange and correlation functional available are listed in Table 2.1.
Table 2.1. A list of exchange and correlation functionals.

(a) Exchange functional

<table>
<thead>
<tr>
<th>Functional</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirac-Slater [47]</td>
<td>LDA</td>
</tr>
<tr>
<td>Von Barth-Hedin [48]</td>
<td>LDA</td>
</tr>
<tr>
<td>Becke [65]</td>
<td>GGA</td>
</tr>
<tr>
<td>Perdew-Wang [65]</td>
<td>GGA</td>
</tr>
<tr>
<td>Perdew-Burke-Ernzerhof [59]</td>
<td>GGA</td>
</tr>
</tbody>
</table>

(b) Correlation functional

<table>
<thead>
<tr>
<th>Functional</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perdew-Zunger [49]</td>
<td>LDA</td>
</tr>
<tr>
<td>Von Barth-Hedin [48]</td>
<td>LDA</td>
</tr>
<tr>
<td>Perdew –Wang [58]</td>
<td>LDA</td>
</tr>
<tr>
<td>Vosko-Wilk Nusair [50]</td>
<td>LDA</td>
</tr>
<tr>
<td>Perdew [55]</td>
<td>GGA</td>
</tr>
<tr>
<td>Lee-Yang-Parr [65]</td>
<td>GGA</td>
</tr>
<tr>
<td>Perdew-wang [58]</td>
<td>GGA</td>
</tr>
<tr>
<td>Perdew-Burke-Erazerhof [59]</td>
<td>GGA</td>
</tr>
</tbody>
</table>

The basic algorithm to find the ground state energy and density of a system of $N$ electron moving in a specific external potential $V_{\text{ext}}(r)$ is thus,

1) The initial guess of the density $n(r)$.
2) Computational of the potential using,
\[ V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int d^3r \frac{\epsilon^2 n(r)}{|r - r'|} + V_{\text{xc}}(n(r)) \]  
(2.17)

3) Find the N lowest eigen values of Schrödinger equations,

\[ E_n \Psi_n = -\frac{\hbar^2 \nabla^2}{2m} \Psi_n + V_{\text{eff}} \Psi_n \]  
(2.18)

4) Get the density from the wave function,

\[ n(r) = \sum_{i=1}^{N} \Psi^*_\omega(r) \Psi_\omega(r) \]  
(2.19)

5) Once again Go back to (2) and repeat until the density and ground state energy cease to change significantly.

6) Compute the ground state energy from,

\[ E = \sum_{i=1}^{N} E_i \]  
(2.20)

On the basis of ground state energy, forces and eigen values, the important properties of the material at normal and ambient conditions in different phases have been predicted. The plane wave pseudopotential approach is thoroughly utilized for the same. The necessary details for the same will be discussed whenever applicable. We have extensively used Quantum Espresso [64] code for the calculation of various ground state and high pressure properties.
The general flow chart of above procedure is given below.

1. Initial Guess
   \[ n \uparrow(r), n \downarrow(r) \]

2. Calculate Effective Potential
   \[ V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_{\text{Hart}}(n) + V_{\text{xc}}(n \uparrow, n \downarrow) \]

3. Solve KS Equation
   \[ \left(-\frac{\nabla^2}{2} + V_{\text{eff}}(r)^\sigma\right)\psi_i^\sigma(r) = E_i^\sigma\psi_i^\sigma(r) \]

4. Calculated Electron Density
   \[ n^\sigma(r) = \sum_i \frac{1}{\rho_i} \left|\psi_i^\sigma(r)\right|^2 \]

5. Self-consistent

   - No
   - Yes

6. Output Quantities
   Energy, Force, Stresses
   Eigen values
2.1.6 Quantum Espresso Package

Quantum Espresso is presently divided into several executables, performing different types of calculations, although some of them have overlapping functionalities. Typically there is single set of functions or a single Fortran 90 module that perform each specific task, but there are still important exceptions to this rule, reflecting the different origin and different styles of the original components. Quantum Espresso has in fact built out of the merging and re-engineering of different packages.

2.1.6.1 PWscf (Plane-Wave Self-Consistent Field)

PWscf implements an iterative approach to reach self-consistency, using iterative diagonalization techniques, in the framework of the plane-wave pseudopotential method.

PWscf can use the well established LDA and GGA exchange-correlation functional, spin-polarization within the scheme proposed in [66] and can treat noncollinear magnetism as e.g. induced by relativistic effect. Self consistency is achieved by relativistic effects [67, 68] or by complex magnetic interactions. DFT + Hubbard $U$ calculations [69] are implemented for a simplified rotationally invariant form [70] for Hubbard term. Self- consistency is achieved via the modified Broyden method of [72]. The sampling of Brillouin Zone can be performed using either special [73, 74] $k$-point provided in input or those automatically calculated starting from a uniform grid. Crystal symmetry are automatically detected and exploited to reduce computational costs, by restricting the sampling of the BZ to the irreducible wedge alone. When only $\Gamma$ point is used, advantage is taken of the real character of the Kohn-Sham orbitals, allowing one to store just half of the Fourier components. BZ integrations in metallic systems can be performed using a variety of smearing techniques. Such as Fermi Dirac, Gaussian, Methfessel-Paxton [75] and Marzari-Vanderbit cold smearing [76]. The tetrahedron method [77] is also implemented. Finite temperature effects on the electronic properties can be easily accounted for by using the Fermi Dirac smearing as a practical way of implementing the Mermin finite-temperature density functional approach [78].

It is used for (i) Self-consistent ground-state energy and Kohn-Sham orbitals, forces, structural optimization (ii) Spin-orbit and non-colinear magnetization (iii) Molecular dynamics on the ground-state Born-Oppenheimer surface (no Car-
Parrinello dynamics) (iv) Variable-cell molecular dynamics with modified kinetic functional (v) NEB and Fourier Strings Method schemes for transition paths, energy barriers.

2.1.6.2 Equation of state

Several forms of EOS have been proposed in literature connecting the pressure to the volume, which are universal, i.e. irrespective of the material considered. Some of them are popular empirical ones Vinet’s EOS for solid under strong compression [80] and one of the earliest one, Birch and Murangun’s EOS [79-83].

In the present work, the calculated total energies were fitted to Murnaghan equation state. In the original form [82-84] Murnaghan’s equation of state comes from the assumption of a linear behavior of the bulk modulus of a solid compressed to a finite strain with respect to pressure. For a fixed number of particles at the absolute zero temperature, the relation between pressure \( P \) and volume \( V \) reads,

\[
P(V) = \frac{B}{B_0} \left( \frac{V}{V_0} \right)^{\frac{6}{5}} - 1
\]

Similarly for the Birch equation, the \( P-V \) relation is,

\[
P(V) = \frac{3}{2} B_0 \left[ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right]
\]

Furthermore, at zero temperature, the pressure may be written as a function of a volume only,

\[
P(V) = -\frac{dE(V)}{dV}
\]

The theoretical equilibrium lattice constant is determined by fitting the total energy as a function of volume to either of the following expression (2.24) and (2.25) formerly renowned as the Murnaghan equation of states (EOS) [81].
\[ E(V) = E_0 - \frac{B_0 V_0}{B - 1} + \frac{B_0 V}{B} \left( \frac{V_0/V}{B - 1} + 1 \right) \]  

(2.24)

and

\[ E(V) = E_0 - \frac{B_0 V_0}{B (B - 1)} \left( B \left( 1 - \frac{V}{V_0} \right) + \left( \frac{V_0}{V} \right)^B - 1 \right) \]  

(2.25)

### 2.1.6.3 Phonons using Density-Functional Perturbation Theory

The phonon package implements density-functional perturbation theory (DFPT) for the calculation of second- and third-order derivatives of the energy with respect to atomic displacements and to electric fields. The global minimization approach is used for the special case of normal modes in finite (molecular) systems, where no BZ sampling is required (Gamma code). In the general case, a self-consistent procedure is used, with the distinct advantage that the response to a perturbation of any arbitrary wave length can be calculated with a computational cost that is of the same order as that of the unperturbed system. Thus, the response at any wave vector, including very small (long-wavelength) ones, can be inexpensively calculated. This later approach and the technicalities involved in the calculation of effective charges and interatomic force constants are described in detail in [84, 85] and implemented in PH code.

Symmetry is fully exploited in order to reduce the amount of computation. Lattice distortion transforming according to irreducible representations of small dimensions are generated first. The charge-density response to these lattice distortions is then sampled at a number of discrete \( k \)-points in the BZ, which is reduced according to the symmetry of the small group of the phonon wave vector \( q \). The grid of the \( q \) points needed for the calculation of inter-atomic force constants reduces to one wave vector per star: the dynamical matrices at the other \( q \) vectors in the star are generated using the symmetry operation of the crystal. This approach allows us to
speed up the calculation without the need to store too much data for summarization. The calculated second-order derivatives of the energy works also for US PPs [86, 87] and for all GGA flavors [88, 89], used in PWscf and in CP. Advanced features of the PHonon package include the calculation of third-order energy derivatives and of electron-phonon or phonon-phonon interaction coefficients. Electron-phonon interactions are straightforwardly calculated from the response of the self-consistent potential to a lattice distortion. This involves numerically sensitive ‘double-delta’ integration at the Fermi energy, which is performed using interpolation on a dense \( k \)-point grid. Interpolation techniques based on Wannier functions [92] will considerably speed up these calculations. The calculation of the harmonic force constants from third-state energy is described in [93] and is performed by a separate code called d3. Static Raman coefficients are calculated using the second-order response approach of [94, 95]. Both third-order derivatives and Raman coefficients calculations are currently implemented only for NC PPs. Thus, using plane wave pseudopotential density functional theory as implemented in Quantum ESPRESSO package, we have calculated various ground state and high pressure properties of materials of interest in solid phase. Further, full phonon dispersion relation is evaluated using density functional perturbation theory.

### 2.1.6.4 Structural phase transitions

The structural phase stability is determined by calculating Gibbs free energies \( G \) for the two phases: [84], which is given by,

\[
G = E_{\text{tot}} + PV + TS
\]  

(2.26)

Since in the theoretical calculations, we need to calculate phase transition at zero temperature, Gibbs free energy equals the enthalpy \( H \),

\[
H = E_{\text{tot}} + PV
\]  

(2.27)

At a given pressure, the stable structure is the one whose enthalpy has the lowest value. The transition pressures is the pressure at which, the enthalpies for the two phases are equal [94-97].
2.2 Model potential formulation for liquids

In the previous section (2.1), we have described the theoretical methods used to calculate various physical properties of solids. Now, we describe the model potential formulation, which is used in the present work to calculate elastic, vibrational, electrical transport and dynamical properties of liquid metals and their alloys.

It is well established that density functional theory can very well reproduce various properties of solids. In case of liquids, due to many body nature of inter-atomic potential, it is quite difficult to calculate physical properties of liquids using density functional theory. On the other hand, model potential formulation, with some experimental data as input, can reproduce very well different physical properties of liquid metals and their alloys. The main limitation of the model potential formulation is that it involves at least one parameter, known as core radius. However, looking to the computational difficulties in determining various physical properties of liquids using any first principles methods or molecular dynamics simulation methods, model potential formulation mimic well different physiochemical properties of liquid metals and their alloys.

Model potential formalism is also known as model pseudopotential formalism, where, the model potential is the weak ion-electron pseudopotential. The term pseudopotential was first used by Fermi in the study of low energy nucleon scattering [99] and it was applied to atoms by Helmann [100]. Phillips and Kleinman [101] and Antonick [102] used it in the energy band structure of solids. Pseudopotential is constructed in two different ways. In the first case, true atomic potential and the corresponding core wave functions have to be included explicitly. In the second way, the pseudopotential is replaced by a model potential having a simple analytical or empirical form. The model pseudopotential is called local pseudopotential, if it depends on the ion positions and it is called nonlocal, if it depends on the energy/momentum also. As nonlocal pseudopotential are energy eigen value dependent, the exact form of non local pseudopotential is quite complicated.

Abarkov and Heine [103] Animalu and Heine [104], Shaw and Harrison [105] used nonlocal pseudopotential. But due to mathematical complexities, nonlocal pseudopotential is not used as much as local pseudopotential. It is different thing, that usage of local pseudopotential may introduce little inaccuracies in results but it will reduce mathematical complexities and calculation time.
2.2.1 Formulation of the model pseudopotential

Since, the conduction electron wave functions are not exactly plane wave near the core we need to represent the set of wave functions in a more modified form. There are many ways to formulate the pseudopotential. Here, the potential is formulated with Orthogonalized Plane Wave Method (OPW’s) [106].

The main task in this theory is to solve Schrödinger equation for the given system using a model potential. The Schrödinger equation is given by (neglecting any external interaction) [107]

\[ H_T \psi_T = E_T \psi_T \] (2.28)

Where, \( H_T \) is the total Hamiltonian given by,

\[ H_T = H_i + H_e \] (2.29)

where, \( H_i \) and \( H_e \) represent the ionic and electronic Hamiltonian respectively.

The OPW’s are written as [106]

OPW’s = Plane wave – core states

If a normalised plane wave be represented by \( |k\rangle \) and the core state is represented by \( \langle e, i |k\rangle \), then we can write the OPW’s as,

\[ |OPW_k\rangle = |k\rangle - \Sigma |e, i\rangle \langle e, i |k\rangle \] (2.30)

Then the OPW’s can be written as

\[ |OPW_k\rangle = (1 - P)|k\rangle \] (2.31)

Here, \( P \) is known as projection operator, which project any function on to the core states. So, that we can determine probable core state. Where, \( | P \rangle = \sum_a |\alpha\rangle \langle \alpha | \)
The expansion of wave function may be written as

\[ \psi_k = \sum_q a_q(k)(1-P)|k+q\rangle \]  

(2.32)

where, \( a_q(k) \) are the expansion coefficients.

Now, let us consider,

\[ \Phi_k = \sum_q a_q(k)|k+q\rangle \]  

(2.33)

\[ \therefore \psi_k = (1-P)\Phi_k \]  

(2.34)

If we use this expansion in the Schrödinger equation (2.1) then we have,

\[ H(1-P)\Phi_k = E(k)(1-P)\Phi_k \]  

(2.35)

\[ \therefore [T+V(r)]\Phi_k - HP\Phi_k = E(k)\Phi_k - E(k)P\Phi_k \]  

(2.36)

By rearranging the terms we have,

\[ \therefore T\Phi_k + [V(r) - H + E(k)]P\Phi_k = E(k)\Phi_k \]  

(2.37)

By introducing

\[ W(r) = V(r) + [E(k) - H]P \]  

(2.38)

We can write

\[ \therefore T\Phi_k + W(r)\Phi_k = E(k)\Phi_k \]  

(2.39)
Where $W(r)$ is known as the ‘Pseudopotential’ and $\Phi_\alpha$ is known as the pseudo wave function.

\[
W(r) = V(r) + \sum_\alpha \left[ (E(k) - E_\alpha) \right] |\alpha\rangle \langle \alpha| \tag{2.40}
\]

Here in the equation (2.40), the second term on the right is repulsive, since the contribution to $W(r)$ come out from the outer region of both the core orbital, so that the difference $E(k) - E_\alpha$ will be large and positive. While the first term due to the true potential felt by the valence electron in the core region of ions is actually strong and attractive. Thus the repulsive contribution cancels the true potential such that the pseudopotential becomes effectively weak. This weak potential can be treated as a perturbation.

A conduction electron will interact with all ions so we may write the pseudopotential $W(r)$ as the sum of the contribution of the spherically symmetric individual ion pseudopotential. Thus we have

\[
W(r) = \sum_i w(|r - r_i|) \tag{2.41}
\]

where $r$ and $r_i$ are the coordinates of the electron and ion respectively.

Hence matrix elements of the pseudopotential can be written using the perturbation expansion as,

\[
\langle k' | W(r) | k \rangle = \frac{1}{\Omega^2} \int \exp(i k' \cdot r) \sum_i w(|r - r_i|) \exp(-i k \cdot r) d^3 r \tag{2.42}
\]

\[
= S(q) W(q) \tag{2.43}
\]

Here we have denoted $k' = k + q$ and introduced the structure factor $S(q)$ and the form factors of the single-site potential $W(q)$.
\[ S(q) = \frac{1}{N} \sum_{i} \exp\left( -i \mathbf{q} \cdot \mathbf{r}_i \right) \] 

(2.44)

The structure factor $S(q)$ is the indirect measure of periodicity of given structure. It can be experimentally determined from x-ray diffraction data. The form factor $W(q)$ is given by,

\[ W(q) = \langle k + q | W | k \rangle \] 

(2.45)

\[ \therefore W(q) = \frac{1}{\Omega_0} \int \exp[-i(k + q).r]W(r)\exp(ik.r)d^3r \] 

(2.46)

Where, $\Omega_0 = \Omega/N$ is the volume per atom. $N$ is total no. of atoms and $\Omega$ is total volume. From, above equations we can say that the matrix element for scattering depends on both the structure factor and the form factor. In other words it depends on the periodicity of the structure and the kind of potential among constituent atoms or ions. The form factor is our Pseudopotential in q-space with screening and exchange and correlation effects included.

### 2.2.2 Dielectric screening

In the theory of metals the assembly of free electrons in the metals is considered as degenerate electron gas with uniform distribution. When an external positive charge is placed in such a system the whole distribution of electrons (density) changes so as to oppose the change in the potential or to maintain the equilibrium. This phenomenon is known as screening of positive charge. Due to screening effects the potential experienced by conduction electrons changes by a large amount. Also, the total displaced charge is equal to charge of the ion [108].

Screening plays very important role in the response of metals to any external field. In order to calculate the effect of screening we need to divide each Fourier component of bare ion potential by dielectric screening function [108,109]

\[ W_s(q) = \frac{W_B(q)}{\varepsilon(q)} \] 

(2.47)
Initially, only static dielectric function was introduced in which direct electron-electron interactions were not included. It was termed as static Hartree dielectric function \[109\]. After that it was corrected by introducing an extra term ‘exchange’ for the requirement of Pauli’s exclusion principle for antisymmetric wave function. Also to get the precise understanding of the dielectric function the correlation effects becomes necessary to introduce.

Where, \( \varepsilon_H(q) \) is static Hartree dielectric function given by \[106\],

\[
\varepsilon_H(q) = 1 + \frac{me^2}{2\pi\hbar k_F Y} \left[ \frac{1 - Y^2}{4Y} \ln \left| \frac{1 + Y}{1 - Y} \right| \right] \tag{2.48}
\]

2.2.3 Exchange and correlation effects

The exchange and correlation effects among conduction electrons are required by Pauli’s exclusion principle. It can be found from many body perturbation theories. Correlation effects arise from the columnic repulsion between the electrons. Such repulsion gives rise to correlation hole around each electron.

The final form of dielectric screening function after the inclusion of exchange-correlation effects is given by,

\[
\varepsilon(q) = 1 + \left[ (\varepsilon_H(q) - 1)(1 - f(q)) \right] \tag{2.49}
\]

Here, \( f(q) \) is the local field correction function. There are many forms of possible local field correction functions which are proposed to incorporate the exchange and correlation effects among conduction electrons. In the present work we have used five different form of local field correction functions viz. Hartree function (H) \[110\], Taylor function (T) \[111\], Ichimaru-Utsumi function (IU) \[112\], Farid et al function (F) \[113\] and Sarkar et al function (S) \[114\].
2.2.4 Local field correction functions

1. Hartree function

The Hartree local field correction function does not involve any kind of exchange and correlation effects. The mathematical expression for this function is given by [110],

\[ f(q) = 0.0 \]  \hspace{1cm} (2.50)

2. Taylor function

The mathematical expression for Taylor screening function [111] is given by,

\[ f(q) = \frac{q^2 \left( 1 + \frac{0.1534}{\pi k_F} \right)}{4k_F^2} \]  \hspace{1cm} (2.51)

This function is quadratic function of q. It is an even function with respect to q. It satisfies the compressibility sum rule. It is able to explain well the exchange and correlation effect.

3. Ichimaru-Utsumi Local field correction function

The IU function satisfies the compressibility sum rule. It gives good results for \( r_s \leq 15 \) compared to the function proposed by Vashistha and Singhvi, which can be used up to metallic density range \( r_s \leq 6.0 \). The mathematical expression for this function is given by, [112]

\[ f(q) = AX^4 + BX^2 + C + \left[ AX^4 + \left( B + \frac{8}{3} A \right) X^2 - C \right] \frac{4 - X^2}{4X} \ln \left( \frac{2 + X}{2 - X} \right) \]  \hspace{1cm} (2.52)

Where, A, B and C are the \( r_s \) dependent parameters and \( X = q/k_F \)

\[ A = 0.029 \]  \hspace{1cm} \( 0 \leq r_s \leq 15 \)
\[ B = \left( \frac{9}{16} \right) \gamma_o - \left( \frac{3}{64} \right) [1 - g(0)] - \left( \frac{16}{15} \right) A \]

\[ C = \left( -\frac{3}{4} \right) \gamma_o + \left( \frac{9}{16} \right) [1 - g(0)] - \left( \frac{16}{15} \right) A \]

\[
\gamma_o = 0.25 - \left( \frac{\pi}{24} \right) \left( \frac{4}{9\pi} \right)^{1/3} r_s^5 \left[ r_s^{-2} \frac{d}{dr_s} E_C(r_s) \right]
\]

and 
\[ g(0) = \frac{Z'}{8I(Z')}, \]

Here \( I_1(Z') \) is the first order modified Bessel’s function and \( E_C(r_s) \) is the correlation energy.

4. Farid et al function

The local field correction function due to Farid et al. is given by [113],

\[
f(q) = AX^4 + BX^2 + C + \left[ (AX^4 + DX^2 - C) \left( \frac{4 - X^2}{4X} \right) \ln \left| \frac{2 + X}{2 - X} \right| \right]
\]

(2.53)

With, \( X = q / k_F \) and A, B, C and D are the \( r_s \) dependent parameters. This function also satisfies the compressibility sum rule.

\[ A = \frac{63}{64} a_0 + \frac{15}{4096} \left[ b_0^A - 2 \left( b_0^B + b_0^C \right) - 16 b_{-2} \right] \]

\[ B = \frac{9}{16} \gamma_o + \frac{7}{16} b_{-2} - \frac{3}{64} b_0 - \frac{16}{15} A \]

\[ C = -\frac{3}{4} \gamma_o + \frac{3}{4} b_{-2} + \frac{9}{16} b_0 - \frac{16}{5} A \]

\[ D = \frac{9}{16} \gamma_o - \frac{9}{16} b_{-2} - \frac{3}{64} b_0 + \frac{8}{5} A \]

\[ b_0 = b_0^A + b_0^B + b_0^C \]

\[ b_0^A = \frac{2}{3} [1 - g(0)] \]
\[ b_0^B \equiv \frac{48E^2_p}{35\omega_p^2} \delta_4 \]
\[ b_0^C \equiv -\frac{16E^2_p}{25\omega_p^2} \left[ 2\delta_2 + \delta_2^2 \right] \]
\[ b_2 \equiv \frac{4E^2_p}{5\omega_p^2} \delta_2 \]
\[ \frac{E^2_p}{\omega_p^2} = \frac{1}{12\lambda^4 r_s} \]
\[ \lambda \rightarrow \alpha = \left( \frac{4}{9\pi} \right)^{1/3} = 0.52106 \]
\[ a_0 = 0.029 \quad (0 \leq r_s \leq 15) \]
\[ \delta_2 = \sum_{j=1}^{6} \xi_j x^j \quad x = r_s^{1/2} \]
\[ \xi_1 = -2.2963827 \times 10^{-3} \]
\[ \xi_2 = 5.6991691 \times 10^{-2} \]
\[ \xi_3 = -0.8533622 \]
\[ \xi_4 = -8.7736539 \]
\[ \xi_5 = 0.7881997 \]
\[ \xi_6 = -1.2707788 \times 10^{-2} \]
\[ \rho_0 = -79.9684540 \]
\[ \rho_1 = -140.5268938 \]
\[ \rho_2 = -35.2575566 \]
\[ \rho_3 = -10.6331769 \]
\[ \frac{\delta_4}{\delta_2} = \frac{\sum_{j=1}^{8} \xi_j x^j}{x^6 + \sum_{j=0}^{8} \rho_j x^j} \]
\[ \xi_0 = 23.0118890 \]
\[ \xi_1 = -64.8378723 \]
\[ \xi_2 = 63.5105927 \]
\[ \xi_3 = -13.9457829 \]
\[ \xi_4 = -12.6252782 \]
\[ \xi_5 = 13.8524989 \]
\[ \xi_6 = -5.2740937 \]
\[ \xi_7 = 1.0156885 \]
\[ \xi_8 = -1.1039532 \times 10^{-2} \]
\[ \rho_0 = 9.5753544 \]
\[ \rho_1 = -32.9770151 \]
\[ \rho_2 = 48.2528870 \]
\[ \rho_3 = -38.7189788 \]
\[ \rho_4 = 20.5595956 \]
\[ \rho_5 = -6.3066750 \]
\[ z = 4 \left( \frac{\alpha r_s}{\pi} \right)^{1/2} = 4 \lambda^{1/2} \]
\[ \lambda = \frac{\alpha r_s}{\pi} \]
\[ g(0) = \frac{1}{8} \left[ \frac{Z}{I_1(Z)} \right]^2 \]

\( I_1(Z) \) is Bessel Function of first kind and first order.

5. **Sarkar-Sen function**

The local field correction function due to Sarkar et al. is given by [114],

\[ f(q) = A \left[ 1 - \left[ 1 + B X^4 \right] \exp(-C X^2) \right] \quad (2.54) \]

Here, \( X = q / k_f \) and A, B and C are \( r_s \) dependent parameters. This function satisfies the compressibility sum rule accurately.

Where A, B and C are as above.
\[ g(0) = \frac{1}{8} \left[ \frac{Z}{I_1(Z)} \right]^2 \]

With
\[ a = 0.0301412 \]
\[ b = -0.0084724176 \]
\[ c = 0.0016291083 \]
\[ d = -0.2386599 \]
\[ e = 0.027960609 \]

Constants A and C are determined from the limiting values of \( f(q) \).

\[ A = \lim_{q \to 0} f(q) = 1 - g(0) \]
and C is found using

\[ \lim_{q \to 0} f(q) = AC \left( \frac{q}{k_F} \right) \]

\[ \therefore \gamma_0 = AC \]

\[ \therefore C = \frac{\gamma_0}{1 - g(0)} \quad \text{With} \]

\[ \gamma_0 = 0.25 - \left( \frac{\pi}{24} \right) \left( \frac{4}{9\pi} \right)^{1/3} \frac{1}{r_s^5} \frac{d}{dr_s} \left[ r_s^{-2} \frac{d}{dr_s} E_s(r_s) \right] \]

The plot of \( f(q) \to q \) for all five local field correction functions is shown in Figure 2.2.
2.2.5 Pseudopotential form factor

In the present study to incorporate the electron-ion interaction, the well established Ashcroft empty core model potential has been used. Using this potential, the elastic, vibrational, electronic transport and dynamical properties of aluminum and its liquid alloys are calculated.

This potential has a form in r-space given by [115].

$$W(r) = \begin{cases} 0.0 & r \leq r_c \\ -\frac{Ze^2}{r} & \text{otherwise} \end{cases}$$  \hspace{1cm} (2.55)$$

The graph of this function has been shown in Figure 2.3.
The fourier transform of this potential in q-space is given by,

\[ W_B(q) = -\frac{4\pi Z e^2}{\Omega \omega^2} \cos(qr_c) \]  

Figure 2.3. r-space variation of empty core model potential.

The graph of this function has been shown in Figure 2.4 along with the screened form factor. To calculate the screened form factor, Taylor function has been used. This potential with the combination of five different local field correction functions has been used to calculate elastic, vibrational, electrical transport and dynamical properties of liquid metals and their alloys.
Figure 2.4. Bare ion (full line) and screened form factor (dashed line) for Aluminium.
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