Chapter 2

2 Theory of Pseudopotential

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2.1 Prologue

Over the past decades, our technological and industrial base has become increasingly dependent on advanced materials. There is every indication that this trend will continue to accelerate, and that progress in many areas will depend increasingly on the development of new materials and processing techniques [2.1].

A second and equally significant trend is the continuing ascent of the information technologies, which now touch almost every aspect of life in some way. Most significant for scientists is the emergence of numerical modeling as a powerful and widely used tool. This has been fueled not only by the increasing performance of state of the art supercomputers but also, and perhaps more importantly, by the availability of relatively inexpensive high performance workstations. In fact, the ubiquitous personal computer has become a capable research tool and all but the most demanding calculations can now be done routinely using widely available PC's and PC clusters. Problems that required the largest supercomputers in the early 1980's can now be solved routinely in almost any location [2.1].

In this environment, it is natural that there is a strong interest in using numerical modeling in materials science. Historically, progress in materials science has almost always occurred through laboratory experimentation, often guided by empirical trends, knowledge of the properties of related materials, and physical and chemical intuition, but less commonly by predictions based on numerical modeling. This is changing [2.1].

First principles simulations, using density functional theory and particularly the local density approximation and generalized gradient approximations, have proved to be a reliable and computationally tractable tool in condensed matter physics. These
simulations have now impacted virtually every area of this broad field. Applications in materials science had, however, remained more elusive, since this is the realm not of the simple ordered stoichiometric solids that are most easily simulated, but of so called "real materials". In other words to apply first principles techniques in materials science it is necessary to treat complex systems, with stoichiometric deviations, surfaces, impurities, grain boundaries and other point and extended defects. However, we are now at the threshold where simulations are starting to make a major impact in this area as well [2.1].

Along with the advances in computing technology that have occurred during the last decade, there have been important algorithmic improvements, particularly for planewave based methods, and for certain classes of materials it is now feasible to simulate systems containing several hundred atoms in a unit cell. This opens the door for the direct application of these techniques in studying a substantial set of real materials problems. Further, it is possible to use first principles calculations to create sophisticated data sets that can parameterize model Hamiltonians. These then can be used to model even more complex materials problems [2.1].

At this time, density functional practitioners are divided into two nearly disjoint communities; one employing pseudopotentials and relatively simple basis sets (particularly planewaves) and the other using methods with complex but efficient basis sets, such as the linearized augmented planewave (LAPW), the linearized muffin-tin orbital (LMTO) and related methods. The latter community has traditionally dominated research on transition metals and their compounds [2.1].

There are signs that this could change. The development of improved algorithms, particularly the Car-Parrinello (CP) and related methods, and of sophisticated ultrasoft pseudopotentials has for the first time made it feasible to
perform accurate simulations of complex transition metal systems using planewave basis sets. Nonetheless, the LAPW, LMTO and related approaches remain the methods of choice for transition metals, and a case can be made that this will continue, especially since the algorithmic improvements, referred to generically as CP, can be incorporated into LAPW and other codes [2.1].

It is our view that a more realistic scenario is that these traditionally distinct approaches will eventually converge. Pseudopotentials bear relationships with the LAPW method, and pseudopotentials corresponding to the LAPW method have been explicitly constructed. It is perhaps not surprising that there are relationships between planewave pseudopotential methods and the LAPW method. Both approaches have a common starting point, i.e. a planewave basis set. Further, both approaches are motivated by the observation that planewaves, by themselves, are ill suited for direct solution of Schrodinger's equation in a crystal. This is because the potential and therefore the wavefunctions are rapidly varying near the nuclei. In the planewave pseudopotential approach, this problem is avoided by replacing the Hamiltonian near the atoms with a smoother pseudo-Hamiltonian in such a way that the valence energy spectrum is reproduced, but the core states are removed, as are the rapid variations in the wavefunctions near the nucleus. In the LAPW method, the planewaves are modified near the atoms rather than the Hamiltonian. This modification (the augmentation) is such that small wavevector ($G$) augmented planewaves can reproduce the rapid variations in the valence wavefunctions. In addition the augmented planewaves are made orthogonal to the core states. Thus, as in the pseudopotential method, the valence energy spectrum is reproduced with a low planewave cutoff, and the core states are removed from the spectrum. In both cases, the basis functions are labeled as planewaves (by $G$), the Hamiltonian matrix elements
are modified in such a way that rapid convergence with the maximum $|G|$ is obtained, and the modification due to an atom is in the vicinity of that atom [2.1].

Condensed matter physics and materials science are concerned fundamentally with understanding and exploiting the properties of interacting electrons and atomic nuclei. This has been well known since the development of quantum mechanics. With this comes the recognition that, at least in principal, almost all properties of materials can be addressed given suitable computational tools for solving this particular problem in quantum mechanics. Unfortunately, the electrons and nuclei that compose materials comprise a strongly interacting many body system, and this makes the direct solution of Schrodinger's equation an extremely impractical proposition. Rather, as was stated concisely by Dirac in 1929, progress depends on the development of sufficiently accurate, but tractable, approximate techniques [2.2].

Thus the development of density functional theory (DFT) and the demonstration of the tractability and accuracy of the local density approximation (LDA) to it defined an important milestone in condensed matter physics. First principles quantum mechanical calculations based on the LDA and extensions, like generalized gradient approximations, have emerged as one of the most important components of the theorist's toolbox. These methods are also starting to have significant impact in many areas of materials science, though there remains much to be done. A real challenge is posed by the highly complex nature of most real materials. Related to this, there has been considerable progress in developing DFT based methods suitable for large systems containing many hundreds of atoms in a unit cell. In addition, widely available user friendly DFT codes, with implementation of many property calculations are available. It seems very reasonable to expect these
trends to continue and for DFT calculations to become ubiquitous tools in materials science [2.1].

A perusal of the electronic structure literature during the late 1970’s and early 1980’s when density functional calculations and particularly ab initio total energy methods were first showing their muscle, reveals that the field was largely dominated by planewave based pseudopotential methods. There is an interesting parallel today. The advent of ab initio molecular dynamics using the Car-Parrinello (CP) method [2.3] has resulted in a considerable leap in the capability of planewave based density functional methods, and application of these approaches has permitted the solution of numerous previously intractable problems. But even now, few substantial applications of these ideas to nonplanewave based methods have been reported. Why?

We think that it is safe to say that the real reasons for the early dominance of planewave methods relate less to computational efficiency than to human efficiency. By this we mean that, because of the extreme simplicity of planewaves, the development and implementation of methods based on them is relatively straightforward. While other methods may have offered significant computational advantages, the extra human effort needed to develop them prevented their early emergence as methods of choice. We think that the situation is similar today, and see no fundamental reason why CP and related algorithms cannot be usefully exploited in non-planewave methods; just that it is more complicated and will take time. Now as then, practitioners of planewave methods are doing good physics while others are developing codes. However, when non-planewave total energy methods became available new areas of computational research were opened up in the $d$- and $f$ band materials, for example. Even today, planewave based CP methods have made little impact on important problems, such as the dynamics of high temperature
superconductors and other correlated materials. Thus it seems quite reasonable to expect that as non-planewave CP-like codes are developed, new vistas will again be opened up, though to what extent remains to be seen.

We begin by reviewing some aspects of planewave pseudopotential.
2.2 Formalism of pseudopotential:

Bloch's theorem, which starts with the periodicity of the crystal lattice, defines the crystal momentum \( k \) as a good (conserved) quantum number and also gives the boundary condition for the single particle wavefunctions, \( \psi_k \). This is

\[
\psi_k (r + R_L) = e^{i k \cdot R_L} \psi_k (r)
\]

(2.1)

where \( R_L \) is a direct lattice vector. The most general solution that satisfies this boundary condition is

\[
\psi_k (r) = e^{i k \cdot r} \sum_G C_G (r) e^{i G \cdot r}
\]

(2.2)

where the \( G \) are reciprocal lattice vectors. However, planewaves are diagonal in the momentum, \( p \), and any powers of the momentum. This means that they are eigenfunctions of the kinetic energy operator \( (p^2/2m) \). Thus we have the solution for the empty lattice (constant potential, which we may choose to be zero). The band energies in Rydberg units are \( (k + G)^2 \) and the wavefunctions are \( e^{i (k+G) \cdot r} \) modulo a normalization. Now suppose that a small periodic perturbation, \( \Delta V(r) \) is added to the Hamiltonian. Then the wavefunctions will no longer be pure planewaves, but mixtures. However, because of the energy denominators that occur in perturbation expansions, the mixture will involve mainly the nearby bands. Thus if our interest is in the lowest few bands, it will not be necessary to include a large number of additional planewaves provided that \( \Delta V(r) \) is weak. Planewaves are ideally suited to the description of this nearly free electron (NFE) situation.

Solids, however, are made up of electrons and nuclei interacting strongly through the Coulomb potential. Nonetheless, according to Fermi liquid theory (FLT) the electronic excitations near the Fermi energy in metals behave as if they were
independent particles. These quasiparticles have renormalized masses and intensities but are non-interacting at sufficiently low energies. Thus, besides its foundational role in the theory of metals, FLT provides guidance for band structure methods as well. That is, that we may expect the Hartree and exchange correlation potentials representing the interaction with the other valence electrons to be weaker than the bare Coulomb interactions would suggest, and perhaps weak enough to justify an NFE based approach in many cases.

This leaves the strong interactions with the core electrons and the nuclei to contend with. In most cases, the core electrons are quite strongly bound, and do not respond effectively to motions of the valence electrons. Thus they may be regarded as essentially fixed.

![Wavefunction comparison](image)

**Figure 2.1** Comparison of a wavefunction in the Coulomb potential of the nucleus (blue) to the one in the pseudopotential (red). The real and the pseudo wavefunction and potentials match above a certain cut off radius $r_c$.

This is the essence of the pseudopotential approximation: The strong core potential (this does not mean $-Ze^2/r$ but rather includes as well the Hartree potential due to the core charge as well as a component of the exchange correlation potential related to the valence-core interaction) is replaced by a pseudopotential, whose
ground state wavefunction $\psi^{PS}$ mimics the all electron valence wavefunction outside a selected core radius. In this way, both the core states and the orthogonalization wiggles in the valence wavefunctions are removed. For many elements, the resulting pseudowavefunctions $\psi^{PS}$ are quite smooth and may be well represented using only low $|G|$ planewaves. Thus planewaves become a simple and reasonably efficient basis for the pseudo-wavefunctions in these cases, and this underlies their popularity. Of course, there is a price to be paid. This is the need to generate and use a pseudopotential, rather than the actual crystal potential. In fact, much of the complexity of the method is transferred from the calculation itself to the generation of the pseudopotential. Further, the core states are fixed in an atomic reference configuration. The frozen core approximation, as it is called, is generally reliable, but breaks down for some elements with extended core states.

The pseudopotential approach originated with the orthogonalized planewave (OPW) method [2.4], in which the valence wavefunctions were expanded using a basis consisting of planewaves that were orthogonalized to the lower lying core states, $\psi_c$

$$\phi_{OPW} (K + G) = \phi_{OPW} (K + G) - \sum_{\alpha, c} \langle \psi_c | \phi_{OPW} (K + G) \rangle \psi_{\alpha, c} \quad (2.3)$$

where $\phi_{PW}$ is a planewave and $\phi_{OPW}$ is the corresponding OPW, and the sum is over core states and atoms.

A pseudopotential related to this may be constructed as follows: Let $H$ be the original Hamiltonian with core and valence wavefunctions, $\psi_c$ and $\psi_v$ respectively. Now consider the pseudostates,

$$\psi^{PS}_c = \psi_v - \sum_{\alpha, c} a_{vc} \psi_{\alpha, c} \quad (2.4)$$
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with \( a_{vc} = \langle \psi_{a,c} | \psi_{v}^{PS} \rangle \). Applying \( H \), we now obtain

\[
H \langle \psi_{v}^{PS} | = \varepsilon_{v} \langle \psi_{v} | + \sum_{a,c} a_{vc} \varepsilon_{c} \langle \psi_{a,c} |
= \varepsilon_{v} \langle \psi_{v}^{PS} | + \sum_{a,c} a_{vc} (\varepsilon_{a,c} - \varepsilon_{v}) \langle \psi_{a,c} |
\]

where \( \varepsilon_{a,c} \) and \( \varepsilon_{v} \) are the core and valence eigenvalues, respectively. Thus, using the definition of \( a_{vc} \),

\[
\left[ H + \sum_{a,c} (\varepsilon_{v} - \varepsilon_{a,c}) \langle \psi_{a,c} | \langle \psi_{a,c} | \right] \psi_{v}^{PS} = \varepsilon_{v} \psi_{v}^{PS}
\]

Therefore the pseudostates satisfy a Schrodinger-like equation with an additional contribution, \( V^{R} \) to the Hamiltonian.

\[
V^{R} = \sum_{a,c} (\varepsilon_{v} - \varepsilon_{a,c}) \langle \psi_{a,c} | \langle \psi_{a,c} |
\]

where \( V^{R} \) differs from a normal potential term in that it is energy dependent through \( \varepsilon_{v} \). Adding \( V^{R} \) to the original potential, \( V \), contained in the Hamiltonian, yields the pseudopotential, \( V^{PS} \),

\[
V^{PS} = V + V^{R}
\]

Outside the core region, \( V^{PS} \) becomes equal to \( V \) as the core wavefunctions vanish. Thus, there is some radius, \( r_{c} \) around an atom beyond which the contribution of that atom to \( V^{R} \) is negligible. Moreover, the construction is linear in the sense that there is a separate and independent additive contribution from each atom \( a \). Most importantly, because of the additional repulsive contribution in the core, the pseudopotential is generally much weaker than the original potential, resulting in reasonable convergence of planewave expansions of the pseudo-wavefunctions.
The term Pseudopotential is defined as “The fictitious / artificial but physically justifiable, weak as well as effective potential experienced by an electron in the vicinity of the ions and cloud of surrounding electrons” [2.5].

Pseudopotential is categorized by their local and nonlocal behaviour. Local potential depends only on the ion positions, while non-local potential depends on the ion position as well as energy/momentum.

The sophistication and efficacy of pseudopotentials have evolved considerably since the Phillips-Kleinman [2.4] construction. This evolution has been driven, at least in large part, by the following goals: (1) First of all the pseudopotential should be as soft as possible, meaning that it should allow expansion of the valence pseudo-wavefunctions using as few planewaves as possible; (2) Secondly, it should be as transferable as possible (meaning that a pseudopotential generated for a given atomic configuration should reproduce others accurately), thereby helping to assure that the results will be reliable in solid state applications, where the crystal potential is necessarily different from an atomic potential; and (3) the pseudo-charge density (the charge density constructed using the pseudo-wavefunctions) should reproduce the valence charge density as accurately as possible. The concept of norm-conservation [2.6, 2.7] represented an important advance in reconciling these conflicting goals.

With norm conserving pseudopotentials, the pseudo-wavefunctions (and potential) are constructed to be equal to the actual valence wavefunctions (and potential) outside some core radius, $r_c$. Inside $r_c$, the pseudo-wavefunctions differ from the true wavefunctions, but the norm is constrained to be the same. That is,

$$\int_0^{r_c} dr \, r^2 |\psi_{PS}^* (r)|^2 = \int_0^{r_c} dr \, r^2 |\psi^* (r)|^2$$

where the wavefunctions refer to the atomic reference state and spherical symmetry is enforced.


2.3 Construction of Model potential:

In solving the Schrödinger equation for condensed aggregates of atoms, space can be divided into two regions with quite different properties. The region near the nuclei, the “core regions”, are composed primarily of tightly bound core electrons which respond very little to the presence of neighbouring atoms, while remaining volume contains the valence electron density which is involved in the bonding together of the atoms. Although the potential in the core is strongly attractive for valence electrons, the requirement that valence wave functions be orthogonal to those of the core produce a large kinetic energy which contributes an effective repulsive potential for valence states [2.8].

Generally, the pseudopotential is set up in a model form in which bare ion potential consisting of certain parameters is developed within certain sphere. In this way, the requirement of core states and exact form of the true potential is bypassed. Usually, the form of repulsive potentials is different in all such pseudopotentials. This potential arises due to the orthogonalisation of conduction band states to core states. In this way, we get splitting of regions about the core [2.5].

The construction of pseudopotential is done either through the direct method [2.9] or empirical method [2.10]. The methods for constructing pseudopotentials have evolved considerably over the years. The initial empirical pseudopotentials were constrained only to reproduce one electron eigenvalues and to be as weak as possible, and these conditions led to non-Hermitian model potentials [2.11]. The Phillips-Kleinman [2.4] procedure was to form valence pseudopotentials by adding small amount of core orbitals of the same symmetry to the valence orbital. The more modern method is to place the emphasis on making the valence pseudo orbital
resemble as much as possible the valence orbital beyond some fiducial core radius and imposes other conditions to complete the assignment.

The earliest introduction of ionic pseudopotentials into self consistent electronic structure calculations occurred in the context of Hartree-Fock and related methods. Since the interest here is primarily in extended condensed matter systems, the fitting of pseudopotentials to experimental data led to the development of “ab-initio” potentials which were parameter free.

In our literature survey we found that numbers of model potentials (like Fiolhais et al model [2.12-2.14], Ashcroft empty core model (AS) [2.15-2.19], Heine-Abarenkov model (HA) [2.16, 2.20, 2.21], Harmonic model potential (HMP) [2.16, 2.20, 2.21], Krasko-Gursky (KG) model [2.22, 2.23], Animalu Heine (AH) model [2.22], Generalized nonlocal model potential (GNMP) [2.24-2.26], energy independent nonlocal model potential (EINMP) [2.8, 2.9], Harrison [2.27-2.28], Weaire [2.29], Brovan and Kagan [2.8], Picket [2.9], Sharma and Kachhawa [2.30], Srivistava and Singh [2.31], Projector Augmented-Wave method (PAW) [2.32, 2.33], Ultrasoft pseudopotentials (USPP) [2.34, 2.35], Troullier-Martins pseudopotentials [2.36] are used to study different properties of metals, liquid metals, semiconductor, alloys, metallic glasses and other disordered phases of materials.

The problem with model pseudopotentials is that of their transferability, because still there is no accurate method to obtain the form factor by which all the properties of liquid metals may be successfully investigated. It is found that a particular pseudopotential may be suitable for some properties of some metals and unsuitable for other properties of other metals. The usefulness of any model potential depends on how many number of parameters it involves. Generally, the potential involving less number of parameters is considered to be, comparatively a better one.
than that involving more number of parameters because it avoids more complexities in the calculation. It has been observed that a unique method of determination of the potential parameter has not been pointed out so far. A number of investigators have used fitting procedure in which the potential parameters are fitted in such a way that a good agreement with experimental findings to be obtained [2.1, 2.37, 2.38]. Such a procedure will generally give good results for a certain property, but the same set of parameters will not give good results for other properties. Hence, we thought it worthwhile to construct a parameter free model potential which, by employing, explains the physical as well as chemical properties of condensed matter.

A pseudopotential method employing a simple model of a solid composed of atomic cores and valence electrons can predict the existence and properties of new solids and their properties [2.39]. By implementing this idea we construct a new model potential by modifying Ashcroft’s empty core model potential [2.15-2.19]. The form of Ashcroft’s empty core model potential [2.15-2.19] is

\[
W_B(r) = \begin{cases} 
0; & r < r_c , \\
-\left(\frac{Ze^2}{r}\right); & r \geq r_c 
\end{cases}
\] (2.10)

The new potential is splitted into three regions [2.40-2.45]

\[
W_B(r) = \begin{cases} 
0; & r < r_j , \\
-\left(\frac{Ze^2}{r}\right) \left(2 - \exp\left(\frac{r}{r_0} - 1\right)\right); & r_j \leq r \leq r_a \\
-\left(\frac{Ze^2}{r}\right); & r > r_a 
\end{cases}
\] (2.11)

Basically, this form of the pseudopotential is the modified version of the Ashcroft’s empty core model [2.15-2.19]. Here we have considered actual core of an ion as an empty core rather than pseudizing it. The whole effective region is splitted into three parts. The effective weak potential felt by an electron is sandwiched
between empty core and long range coulomb potential which is continuous at \( r = r_a \) and is considered between the ionic radius \((r_i)\) and atomic radius \((r_a)\). It may be noted that most of the pseudopotentials [2.12-2.29] are represented always by two-fold splitting in their influence. In the present potential, we have included both the features of the pseudopotential – cancellation as well as weak remaining interaction around the ion. Another important part of the model potential is that it is parameter free. Looking to the success of present approach, we believe that it should be interesting to try out all the local forms of the pseudopotential on the line of the present approach.

In the reciprocal space, the corresponding bare-ion form factor of Ashcroft model potential and present model potentials are respectively as follow,

\[
W_B(q) = \frac{-4 \pi z e^2}{q^2 \Omega} \cos(q \cdot r_c) \quad (2.12)
\]

And

\[
W_B(q) = \frac{-4 \pi z e^2}{q^2 \frac{r_i}{\Omega_{(1+r_i^2)}}} \left[ 2 \left( 1 + 2q^2 r_i^2 \right) \sin(qr_i) - qr_i \left( 1 + 3q^2 r_i^2 \right) \cos(qr_i) + \right]
\times \left[ 2 \left( 1 + 2q^2 r_i^2 \right)^2 \left( qr_i \cos(qr_i) - \sin(qr_i) \right) - \right.
\exp \left( \frac{r_i}{r_a} - 1 \right) \left\{ \left( -2q^2 r_i^3 + q^3 r_i^3 r_i^1 + q^4 r_i^4 r_i^1 \right) \cos(qr_i) - \right.
\left. \left( -2q^2 r_i^3 + q^3 r_i^3 r_i^1 + q^4 r_i^4 r_i^1 \right) \sin(qr_i) \right\} \right]
\quad (2.13)
\]

Here \( Z, e, \Omega, q, r_i \) and \( r_a \) are the valency, electronic charge, atomic volume, wave vector, ionic radius and atomic radius respectively.

The present model potential gives correct limiting values at \( q \to 0 \) and \( q \to \infty \) as follows,

\[
\lim_{q \to 0} W_B(q) = \frac{2\pi z e^2}{3\Omega r_a } \left[ 5 r_i^3 + 4 r_i^3 - 6 r_a \exp \left( \frac{r_i}{r_a} - 1 \right) \left( 2 r_a^2 - 2 r_i^2 r_i^2 + r_i^2 \right) \left( 2 r_a^2 - 2 r_i^2 r_i^2 + r_i^2 \right) \right] \quad (2.14)
\]

And

\[
\lim_{q \to \infty} W_B(q) = 0 \quad (2.15)
\]
2.4 Concept of Screening:

It is necessary to account following major effects while constructing local pseudopotentials [2.46].

- The interactions between electrons with ions which is represented by bare ion local pseudopotential $W_B(q)$.
- Another interactions of an electrons with other conductions electron which is represented by Hartree screening effects $W_S(q)$.
- The role of exchange and correlation effect $W_X(q)$.

Hence the local pseudopotential becomes,

$$W(q) = W_B(q) + W_S(q) + W_X(q)$$  \hspace{1cm} (2.16)

The pseudopotential represents electron ions interaction. To form a metal we have to assemble these electrons and ions. At that time we must consider the interaction between the valence or conduction electron. Hartree approximation [2.27, 2.28] is used to solve this problem, in which each electron moves in a self consistent field determined from the average potential of all other electrons as well as the ion potentials.

When an ion is placed in a free electron gas, the electron density around it changes. The total displaced charge is equal to the charge of the ion i.e. the potential is screened by the electron gas. This effect can be included through dielectric function. It plays a vital role to evaluate the self consistent potential due to the screening of electron gas.

As we have already constructed bare ion pseudopotential $W_B(q)$ and by solving the $W_S(q)$ and $W_X(q)$ one can get the form of $W(q)$ as follow [2.27, 2.28],

$$W(q) = \frac{W_B(q)}{\varepsilon(q)}$$  \hspace{1cm} (2.17)
Where $\varepsilon(q)$ is called dielectric function.

In the beginning, only static dielectric function was introduced which neglect any direct electron-electron interaction. It was Hartree dielectric function [2.27, 228]. The coulomb repulsive force acts between any pair of conduction electrons in a real metal and, hence, they cannot behave independently but tend to keep apart from one another. The repulsive electron–electron interaction is called the coulomb correlation. However, the Pauli’s exclusion principle is included so that two electrons with parallel spins are not allowed to occupy the same position. In other words, a kind of repulsive interaction, which is different from the coulomb correlation, is taken into account between electrons with parallel spins. This is called the exchange energy. These two effects are neglected in Hartree approximation. Thus to introduce exchange and correlation effect into the potential, a modified dielectric function is formed [2.28].

$$\varepsilon(q) = 1 + [1 + \varepsilon_H(q)] [1 - f(q)]$$ \hspace{1cm} (2.18)

From equation (2.27), we see that unscreened potential is converted into screened potential by dividing it by modified dielectric function $\varepsilon(q)$. Here exchange and correlation effects are included through local field correction function $f(q)$. The term $\varepsilon_H(q)$ is called static Hartree dielectric function for free electrons of the form,

$$\varepsilon_H(q) = 1 + \frac{me^2}{2\pi k_F^2 \hbar^2} \left[ \frac{1 - Y^2}{Y^2} \ln \left| \frac{1 + Y}{1 - Y} \right| + 1 \right]$$ \hspace{1cm} (2.19)

Here $k_F$ is the Fermi wave vector, $Y = \frac{q}{2k_F}$, $\hbar = \frac{h}{2\pi}$, $h$ is Planck constant.

The static Hartree dielectric function $\varepsilon_H(q)$ is time independent dielectric function and depends only upon the magnitude of $q$. Also it does not include any kind of exchange and correlation effects.
The local field correction function \( f(q) \) is used to incorporate exchange and correlation effects. In present study we have used seven local field correction functions like Hartree (H) [2.27, 2.28], Hubbard–Sham (HS) [2.47, 2.48], Vashishta–Singwi (VS) [2.49], Sarkar et al (S) [2.50], Taylor (T) [2.51], Ichimaru–Utsumi (IU) [2.52], Farid et al (F) [2.53].

The Hartree (H) [2.27, 2.28] local field correction function is purely a static function, which is defined as,

\[
f_H(q) = 0
\]  
(2.20)

The Hubbard–Sham (HS) [2.47, 2.48] local field correction function is defined as,

\[
f_{HS}(q) = \frac{q^2}{2(q^2 + k_F^2 + k_{TF}^2)}
\]  
(2.21)

Where \( k_{TF} \) is Thomas Fermi wave vector.

Vashishta–Singwi [2.49] local field correction function is expressed as follow,

\[
f_{VS}(q) = A_{VS} \left[ 1 - \exp \left( -B_{VS} \left( \frac{q}{k_F} \right)^2 \right) \right]
\]  
(2.22)

Constants \( A_{VS} \) and \( B_{VS} \) are well defined in reference [2.49].

The Sarkar et al [2.50] local field correction function is defined as follow,

\[
f_{S}(q) = A_{S} \left[ 1 - \left( 1 + B_{S} X^4 \right) \right] \exp \left( -C_{S} X^2 \right)
\]  
(2.23)

Here constant \( A_{S}, B_{S} \) and \( C_{S} \) are given in the reference [2.50].

The screening function due to Taylor (T) [2.51] is expressed as,

\[
f_T(q) = \left( \frac{q^2}{4k_F^2} \right) \left[ 1 + \frac{0.1534}{\pi k_F} \right]
\]  
(2.24)

The Ichimaru & Utsumi dielectric function [2.52] is defined as,
\( f_{IU}(q) = A_{IU} X^4 + B_{IU} X^2 + C_{IU} + \left[ A_{IU} X^4 + \left( B_{IU} + \frac{8 A_{IU}}{3} \right) X^2 - C_{IU} \right] \left[ 4 - \frac{X^2}{4X} \right] \ln \left[ \frac{2 + X}{2 - X} \right] \) \( (2.25) \)

Where \( X = \frac{q}{k_F} \). \( A_{IU} \), \( B_{IU} \) and \( C_{IU} \) are defined in reference [2.52].

The Farid et al [2.53] screening function is defined as follows,

\[
f_F = A_F \left( \frac{q}{q_f} \right)^4 + B_F \left( \frac{q}{q_f} \right)^2 + C_F + \left[ A_F \left( \frac{q}{q_f} \right)^4 + D_F \left( \frac{q}{q_f} \right)^2 - C_F \right] \left[ 4 - \frac{q}{q_f} \right]^2 \ln \left[ \frac{2 - q}{2 + q} \right] \]

\( (2.33) \)

Where \( q_f = \left( \frac{1}{\lambda r_s} \right) \) and \( \lambda = (4/9\pi)^{1/3} \). Here constants \( A_F \), \( B_F \), \( C_F \) and \( D_F \) are described in reference [2.53].

The nature of local field correction functions \( f(q) \) are plotted in Figure (2.2) for liquid Ag. The modified dielectric function \( \varepsilon(q) \) with different local field correction functions \( f(q) \) is plotted in Figure (2.3) for liquid Ag.

From Figure (2.2), it is noticed that the local-field correction function approaches to zero as \( q \to 0 \).

From Figure (2.3), it is found that the inclusion of various local field correction functions to the modified dielectric function \( \varepsilon(q) \) suppresses the static Hartree (H) dielectric function in the entire range of wave vector \( q \). The inclusion of Taylor (T) local field correction [2.51] suppresses more the modified dielectric function \( \varepsilon(q) \) than the other local field correction functions \( f(q) \). The effect of local field corrections \( f(q) \) is more prominent for small values of \( q \).
Figure 2.2 Local field correction functions $f(q)$ for Ag liquid metal
Figure 2.3 Modified dielectric functions $\varepsilon(q)$ for Ag Liquid metals
The input parameters used in the calculation are tabulated in Table (2.1) for transition liquid metals.

**Table 2.1 The input parameters used in the calculation**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Z</th>
<th>Ionic radius ( r_i ) (au)</th>
<th>Atomic radius ( r_a ) (au)</th>
<th>Density (gm/cm(^3))</th>
<th>T (K)</th>
<th>( \Omega ) (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>3</td>
<td>1.5312</td>
<td>3.0359</td>
<td>2.92</td>
<td>1833</td>
<td>172.673</td>
</tr>
<tr>
<td>Ti</td>
<td>4</td>
<td>1.2854</td>
<td>2.7372</td>
<td>4.15</td>
<td>1973</td>
<td>129.398</td>
</tr>
<tr>
<td>V</td>
<td>5</td>
<td>1.1153</td>
<td>2.4783</td>
<td>5.36</td>
<td>2173</td>
<td>106.593</td>
</tr>
<tr>
<td>Cr</td>
<td>3</td>
<td>1.2098</td>
<td>2.3611</td>
<td>6.27</td>
<td>2173</td>
<td>93.008</td>
</tr>
<tr>
<td>Mn</td>
<td>2</td>
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<td>2.5841</td>
<td>5.97</td>
<td>1533</td>
<td>103.209</td>
</tr>
<tr>
<td>Fe</td>
<td>3</td>
<td>1.2098</td>
<td>2.3459</td>
<td>7.01</td>
<td>1833</td>
<td>89.352</td>
</tr>
<tr>
<td>Co</td>
<td>2</td>
<td>1.3989</td>
<td>2.3686</td>
<td>7.70</td>
<td>1823</td>
<td>85.618</td>
</tr>
<tr>
<td>Ni</td>
<td>2</td>
<td>1.3611</td>
<td>2.3554</td>
<td>7.72</td>
<td>1773</td>
<td>62.693</td>
</tr>
<tr>
<td>Cu</td>
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<td>2.4159</td>
<td>7.97</td>
<td>1423</td>
<td>89.423</td>
</tr>
<tr>
<td>Zn</td>
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<td>1.3989</td>
<td>2.5236</td>
<td>6.91</td>
<td>723</td>
<td>106.117</td>
</tr>
<tr>
<td>Zr</td>
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<td>1.4934</td>
<td>3.0057</td>
<td>5.93</td>
<td>2173</td>
<td>172.534</td>
</tr>
<tr>
<td>Pd</td>
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<td>1.6257</td>
<td>2.6011</td>
<td>10.50</td>
<td>1853</td>
<td>113.672</td>
</tr>
<tr>
<td>Ag</td>
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<td>2.7316</td>
<td>9.27</td>
<td>1273</td>
<td>130.507</td>
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<tr>
<td>Cd</td>
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<td>1.8336</td>
<td>2.8148</td>
<td>7.954</td>
<td>623</td>
<td>158.504</td>
</tr>
<tr>
<td>Pt</td>
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<td>1.3233</td>
<td>2.5955</td>
<td>18.70</td>
<td>2053</td>
<td>117.001</td>
</tr>
<tr>
<td>Au</td>
<td>1</td>
<td>1.7202</td>
<td>2.7259</td>
<td>17.20</td>
<td>1423</td>
<td>128.436</td>
</tr>
<tr>
<td>Hg</td>
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<td>2.0794</td>
<td>2.8412</td>
<td>13.55</td>
<td>293</td>
<td>166.031</td>
</tr>
</tbody>
</table>

The bare-ion potential \( W_B(q) \) (in \( r \)-space) [2.40-2.45] for liquid transition metals viz; are plotted in Figures (2.4) to (2.6) along with Ashcroft empty core model [2.15 - 2.19].
Figure 2.4 The Ashcroft and present model potentials in real space for Sc, Ti, V, Cr, Mn and Fe liquid metals.
Figure 2.5 The Ashcroft and present model potentials in real space for Co, Ni, Cu, Zn, Zr and Pd liquid metals
Figure 2.6 The Ashcroft and present model potentials in real space for liquid Ag, Cd, Pt, Au and Hg metals
From Figures (2.4) to (2.6), it is found that the pseudo core of the present model potential [2.40 - 2.44] remains same while depth of the present model potential is reduced compare to the Ashcroft model potential [2.15 – 2.19]. Also the present model potential [2.40 – 2.45] becomes weaker than Ashcroft model potential [2.15-2.19]. Hence, as a result this supports the small core approximation which is essential in the formulation of pseudopotential. The values of $W_B(r)$ at $r = r_i$ are tabulated in Table (2.2).

**Table 2.2** The value of $W_B(r)$ at $r = r_i$ (au)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Present model</th>
<th>Ashcroft model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>-2.7487</td>
<td>-3.9185</td>
</tr>
<tr>
<td>Ti</td>
<td>-4.1258</td>
<td>-6.2237</td>
</tr>
<tr>
<td>V</td>
<td>-5.7420</td>
<td>-8.9662</td>
</tr>
<tr>
<td>Cr</td>
<td>-3.5219</td>
<td>-4.9595</td>
</tr>
<tr>
<td>Mn</td>
<td>-2.0735</td>
<td>-2.6450</td>
</tr>
<tr>
<td>Fe</td>
<td>-3.5395</td>
<td>-4.9595</td>
</tr>
<tr>
<td>Co</td>
<td>-2.2561</td>
<td>-2.8594</td>
</tr>
<tr>
<td>Ni</td>
<td>-2.2830</td>
<td>-2.9388</td>
</tr>
<tr>
<td>Cu</td>
<td>-2.2414</td>
<td>-2.9388</td>
</tr>
<tr>
<td>Zr</td>
<td>-2.1550</td>
<td>-2.8594</td>
</tr>
<tr>
<td>Zn</td>
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<td>-5.3569</td>
</tr>
<tr>
<td>Pd</td>
<td>-2.0187</td>
<td>-2.4605</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.8202</td>
<td>-0.8397</td>
</tr>
<tr>
<td>Cd</td>
<td>-1.8393</td>
<td>-2.1815</td>
</tr>
<tr>
<td>Pt</td>
<td>-4.2765</td>
<td>-6.0455</td>
</tr>
<tr>
<td>Au</td>
<td>-0.9601</td>
<td>-1.1627</td>
</tr>
<tr>
<td>Hg</td>
<td>-1.7390</td>
<td>-1.9236</td>
</tr>
</tbody>
</table>

The form factors of present model potential [2.40 - 2.45] due to different local field correction functions $f(q)$ and Ashcroft model potential [2.15-2.19] due to Sarkar *et al* [2.49 ] are plotted in Figures (2.7) to (2.10) for 3d (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn), 4d (Zr, Pd, Ag and Cd) and 5d (Pt, Au and Hg) liquid transition metals.
Figure 2.7 Form factors for Ashcroft and present model potentials of Sc liquid metal
Figure 2.8 Form factors for Ashcroft and present model potentials of Ti, V, Cr, Mn, Fe and Co liquid metal.
Figure 2.9 Form factors for Ashcroft and present model potentials of Ni, Cu, Zn, Zr, Pd and Ag liquid metal
From Figures (2.7)-(2.10), it is seen that the present model potential has the upper hand over the Ashcroft model potential. A study of the form factors gives a correct limiting value of $(2/3) E_F$ as $q \to 0$ which is required for a local pseudopotential [2.4]. All the form factors are free from unnecessary oscillations at large $q$ values. It is also found that the effect of exchange and correlation is dominant at small $q$ values. The form factors due to our model potential are then employed to investigate the static, dynamic, vibrational and electronic properties of some $d$ shell liquid transition metals in the next part of the thesis.

Figure 2.10 Form factors for Ashcroft and present model potentials of Cd, Pt, Au and Hg liquid metal
References: