2.1 The Pseudopotential theory

2.1.1 Introduction

Pseudopotential method is basically a method to calculate energy band structure and is one of the most popular techniques among the solid state physicist to study various properties of metals, semiconductors, alloys, compounds and non-crystalline substances like metallic glasses and liquids. This tool accurately explains three types of properties; among these, the first type is associated with the value of the total crystal energy or some of its components. The second type involves the properties related to how a solid respond to the external influences like pressure/heat, this property generally involves external transition between the states. The third properties are related to internal energies/vibrations also known as phonons inside the matter.

An electron inside an atom experiences a force due to the nucleus and also due to other electrons in the atom. In the study of condensed matter and its behavior, the main problem is to determine these forces experienced by an electron revolving around the nucleus in certain "preferred" orbits. In this context, Bardeen was the first in the year 1937, who had [2.1] explained the average interaction experienced by an electron through the idea of self-consistent screening. Latter on this idea was applied to investigate several properties of solids [2.2] which is now known as pseudopotential theory. It is an advancement of earlier one electron theory of solids. Ultimately, this theory became a building block for the electronic structural studies of materials.

The starting of this revolutionary idea begins with the One-electron theory. This theory was proposed in the perspective for finding the energies of electron levels inside the solid. The concise historical background of this theory is briefly described below.

The electrical nature of the electron in the form of classical theory of solids was first of all suggested by Ricke [2.3] around twentieth century, which was latter on advanced by Sommerfeld [2.4] with quantum mechanical aspects and with plasma concepts. It is quite remarkable that the plasma theory developed for gases has been applied latter for understanding its effects on the solids. The basis of modern theories of solids is the Sommerfield's theory of free electrons and the dynamics of a crystal may be described on the basis of the one-electron theory. Herein modest structure of one electron model, the
movement of each electron is considered separately in the average field of the nuclei and all the other electrons. Such effects on each electron may be determined by using a self-consistent field method.

In the twentieth century around 1960 the revived form of free electron theory of solids has given a new direction to the studies of condensed matter which is known as Pseudopotential theory. The basic concepts of pseudopotential formalism in crystals were formulated by Phillips and Kleinman [2.5].

Since the solid is made of crystal and hence is made up of electrons and heavy nuclei. For simplicity we can divide the whole crystal into two parts. The first part which contains nuclei and the electrons which are in the completely filled shells, known as "core region" and the second part which consist the "valence electrons". The fundamental concept involved in a pseudopotential calculation is that the ion core can be neglected.

The Schrödinger’s equation which contains the essential features of the behavior of electrons in metallic systems can be written as

\[
H\psi_k = E(k)\psi_k = [T + V(r)]\psi_k
\]  

(2.1)

Where \( T \) is the kinetic energy, \( V(r) \) is the potential energy and \( E(k) \) is the total energy of the system.

For systems with few of electrons it is possible to solve the Schrödinger equation exactly. But for systems with a large number of electrons it is still not possible to solve this equation exactly even with modern computers or supercomputers. For many systems, the deeply bound core electrons serve merely as placeholder and only a few valance electrons participate in the chemical process of interest. Pseudopotential theory takes an advantage of this fact to reduce the dimensionality of a multi-electron chemical problem, the Schrödinger equation is solved only for the valance electrons, and the effects of the core electrons are included implicitly via an additional/extra term in the Hamiltonian. Phillips and Kleinman [2.5] demonstrated that it is possible to derive a pseudopotential that gives an assurance that the valance electron wave function is orthogonal to the core electron wave functions.
2.1.2 Concept of pseudopotential:

The concept of pseudopotential is easily understood by using Orthogonalized Plane Wave (OPW) of wave number \( k \) \([2.1–2.12]\) i.e.

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

(2.2)

Here \( |P\rangle \) is the projection operator given by \( |P\rangle = \sum_\alpha |\alpha\rangle\langle \alpha| \). We may expand the conduction-band state in terms of a general linear combination of OPW's:

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

(2.3)

Now, let us assume

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

(2.4)

Therefore, \( \psi_k = (1 - P)\Phi_k \) \( (2.5) \)

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

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

(2.6)

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

(2.7)

By rearranging the terms we have,

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

(2.8)

by introducing

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

(2.9)

we have

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

(2.10)
Here \( W(r) \) is known as the ‘pseudopotential’ and \( \Phi_\kappa \) is known as the pseudowavefunction.

\[
W(r) = V(r) + \sum_\alpha [E_\kappa - E_\alpha] \langle \alpha | \langle \alpha | r \rangle
\tag{2.11}
\]

In above equation (11), the second term on the right is repulsive, since the contribution to \( W(r) \) comes out from the outer region of both the core orbitals, so that the difference \( E_\kappa - E_\alpha \) 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 in reality strong and attractive. Consequently the repulsive contribution cancels the true potential such that the pseudopotential becomes effectively weak \([2.1-2.12]\). This weak potential is also treated as a perturbation.

An electron at any point \( r \) will interact with all ions situated at the lattice site \( r_i \) and so it is assumed to write pseudopotential \( W(r) \) as the sum or superposition of the spherically symmetric individual ion pseudopotential. Thus,

\[
W(r) = \sum_i W([r - r_i])
\tag{2.12}
\]

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

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

\[
= S(q) W(q)
\tag{2.13}
\]

We have denoted \( \kappa' = k + q \) and introduced the structure factor \( S(q) \) and the form factors of the single-site potential \( W(q) \).

\[
S(q) = \frac{1}{N} \sum_i \exp(-i q \cdot r_i)
\tag{2.14}
\]

\[
W(q) = \langle k + q | W | k \rangle = \frac{1}{\Omega_0} \int \exp[-i(k + q) \cdot r] W(r) \exp(i \kappa \cdot r) d^3 r
\tag{2.15}
\]

Where, \( \Omega_0 = \Omega/N \) is the atomic volume.
As mentioned earlier this potential (pseudo) $W(q)$ may be either local or non-local. Both the non-local pseudopotential and local form of pseudopotential gives accurate prediction for the properties of materials [2.13]. Particularly, the non-local pseudopotentials are energy Eigen value dependent, so the exact form of pseudopotential is quite complicated and therefore cumbersome in formulating it. The local pseudopotentials are position dependent only and hence are preferred mostly [2.14].

### 2.1.3 The screening theory

The phenomenon of screening is the simplest and most important manifestations of electron-electron interactions. In formulating metallic properties a degenerate electron gas with a uniform neutralizing background has been used. When a positive charge is placed in the electron gas, it attracts electrons and creates a surplus of negative charge in its neighborhood and screens the positive charge. The total displaced charge is equal to the charge of the positive ion. Thus the potential is screened by the electron gas. In a real crystal, the electrons which screen the potential are not free.

The effect of screening can be included by dividing the bare-ion potential by a factor which $\varepsilon(q)$ which is called the dielectric screening function. Hence the modified potential is called a screened potential $W_s(q)$ given by

$$W_s(q) = \frac{W(q)}{\varepsilon(q)}$$

(2.16)

The dielectric screening plays a very important role in the evaluation of self-consistent potential due to the screening of the electron gas. Initially, only static dielectric function was introduced in which direct electron-electron interactions were not included. It was termed as static Hartree dielectric function [2.2, 2.4-2.6]. 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. Thus introducing the exchange and correlation effects to the potential, the modified dielectric function is given by [2.2-2.6]

$$\varepsilon(q) = 1 + [\varepsilon_H(q) - 1][1 - f(q)]$$

(2.17)

Here the function $\varepsilon_H(q)$ is called the static Hartree dielectric function for free electrons and $f(q)$ is the local field correction function. The Hartree dielectric screening function is given by
\[ \epsilon_{H}(\mathbf{q}) = 1 + \frac{m e^2}{2 \pi k_F \hbar^2 \eta^2} \left[ \frac{1 - \eta^2}{2\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| + 1 \right] \]  

\[(2.18)\]

Where, \( \eta = \frac{q}{2k_F} \)

It includes exchange and correlation effect in the screening through local field correction function \( f(q) \). The local field correction function \( f(q) \) is a very important factor for establishing a well local pseudopotential and for the proper reproduction of the property under investigation. Now, the electrons interact with each ion through a local pseudopotential \( W^0(r) \) which includes the coulomb potentials of the ion. The sum of potentials due to the ions is

\[ W^0(r) = \sum_j W^0(r - r_j) \]  

\[(2.19)\]

Suppose the potential due to the conduction electrons is \( W^1(r) \). Then the total potential is given by

\[ W(r) = W^0(r) + W^1(r) \]  

\[(2.20)\]

Here \( W^1(r) \) can be determined from the self consistent field method. The first order wave functions is given by

\[ \varphi_k = \sum_q a_q(k) |k + \mathbf{q}\rangle \]  

\[(2.21)\]

Using these first order wave functions we can calculate the electron density. The probability distribution to first order is given by

\[ \varphi^* \varphi = \frac{1}{\Omega} \left[ 1 + \sum_q \{a_q(k)e^{iqr} + a_q^*(k)e^{-iqr}\} \right] \]  

\[(2.22)\]

The total electron density is,

\[ n(r) = \left[ \frac{2}{(2\pi)^3} \right] \sum_q \int d^3k \left\{ a_q(k)e^{iqr} + a_q^*(k)e^{-iqr} \right\} \]  

\[(2.23)\]

Now in terms of Fourier component the electron density of equation (2.23) becomes,

\[ n(r) = \sum_q n_q e^{iqr} \]  

\[(2.24)\]

Where,

\[ n_q = \left[ \frac{2}{(2\pi)^3} \right] \int d^3k \left\{ a_q(k) + a_q^*(k) \right\} \]  

\[(2.25)\]

Here,
\[ a_q(k) = \frac{\langle k + q | W | k \rangle}{\left( \frac{\hbar^2}{2m} \right) \left( k^2 - |k + q|^2 \right)} \]  

(2.26)

Now integrating equation (2.25) using standard integral forms, we get

\[ n_q = \frac{m k_F}{2 \pi^2 \hbar^2} \left\langle k + q \right| W \left| k \right\rangle \left[ \frac{1 - \eta^2}{2 \eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| + 1 \right] \]  

(2.27)

Here the obtained electron density is in terms of the total potential. Now we calculate the screening potential in terms of the electron density. The electrostatic potential satisfies the Poisson’s equation in the form,

\[ \nabla^2 \varphi = -4 \pi \rho \]  

(2.28)

where \( \rho \) is the charge density. Converting into a relation between Fourier components of the screening potential and electron densities, we get

\[ W_s(q) = \frac{4 \pi e^2}{q^2 - n_q} \]  

(2.29)

We eliminate \( n_q \) and solve \( \left\langle k + q \right| W \left| k \right\rangle \) in terms of the unscreened matrix element. We get the result in the form of

\[ \langle k + q | W | k \rangle = \frac{\langle k + q | W^0 | k \rangle}{\varepsilon_{ii}(q)} \]  

(2.30)

also it can be written as

\[ W_s(q) = \frac{W_q(q)}{\varepsilon_{ii}(q)} \]  

(2.31)

Thus, from equation (2.31), it is clear that the screened potential can be obtained from the unscreened potential by simply dividing it by \( \varepsilon_{ii}(q) \) which is time independent dielectric function and depends only upon \( q \). It does not include any kind of exchange and correlation effects.

To include the exchange and correlation effects in the screening theory, we assume that there exists an average interaction \( I(q) \) within the electron gas.

\[ W_X(q) = I(q) n_q \]  

(2.32)

If the electron energies are considered to second order and the wave function to first order in perturbation theory, it is possible to obtain
\[ n_q = \frac{q^2 W(q)}{4\pi e^2} \left[ 1 - \varepsilon_H(q) \right] \] (2.33)

After substitutions of equation (2.27) and equation (2.29) in equation (2.30) we obtain

\[ W(q) = W_h(q) + \frac{4\pi e^2}{q^2} n_q + I(q) n_q \] (2.34)

Using equation (2.27) in equation (2.31) we get

\[ W(q) = W_h(q) + \frac{4\pi e^2}{q^2} \frac{q^2 W(q)}{4\pi e^2} \left[ 1 - \varepsilon_H(q) \right] + I(q) \frac{q^2 W(q)}{4\pi e^2} \left[ 1 - \varepsilon_H(q) \right] \] (2.35)

\[ = W_h(q) + W(q) \left[ 1 - \varepsilon_H(q) \right] \left[ 1 + \frac{q^2 I(q)}{4\pi e^2} \right] \]

Suppose, \( f(q) = -\frac{q^2 I(q)}{4\pi e^2} \) (2.36)

Using equation (2.36) in equation (2.35) we obtain

\[ W(q) = W_h(q) - W(q) \left[ \varepsilon_H(q) - 1 \right] \left[ 1 - f(q) \right] \] (2.37)

\[ W(q) = \frac{W_h(q)}{1 + \left[ \varepsilon_H(q) - 1 \right] \left[ 1 - f(q) \right]} \] (2.38)

Hence we can write

\[ W(q) = \frac{W_h(q)}{\varepsilon(q)} \] (2.39)

Where \( \varepsilon(q) \) is given by equation (2.17).

### 2.1.4 Form factors and Model Potentials

The local field correction function \( f(q) \) is a very important factor for establishing a well local pseudopotential and for the investigation of the properties of matter. The exchange and correlation interaction have been investigated extensively previously for the free electron gas using many body perturbation theory. As noted above the Hartree approximation neglects any direct electron-electron interactions. In particular, the neglect of the requirement of the Pauli Exclusion Principle for anti-symmetric wave functions is corrected in the Hartree-Fock approximation which gives an extra exchange term in the energy. Correlation effects arise from the Coulomb repulsion between electrons, leading to the concept of a ‘correlation hole’ around each electron, which excludes other electrons.
In the present investigation, the most fascinating and more advanced local–field correction functions due to Taylor (T) [2.15], Itchimaru and Utsumi (IU) [2.16], Sarkar-Sen (SS) et al. [2.17], Farid (F) et al. [2.18], are used to introduce exchange and correlation effects. These local field correction functions are discussed below:

As the H[2.2, 2.4-2.6] dielectric is purely be static one and does not include exchange and correlation effects, the local–field correction becomes

\[ f_{H}(q) = 0. \]  

(2.40)

Taylor [2.15] has suggested a very simple expression for \( f(q) \), which satisfies the compressibility sum rule and, in general, covers the overall features of local–field correction function proposed before 1972. According to Taylor [2.15],

\[ f_{T}(q) = \frac{q^3}{4k_F^2} \left[ 1 + \frac{0.1534}{\pi k_F^2} \right]. \]  

(2.41)

The local–field function of IU [2.16] is a fitting formula for the dielectric screening function of the degenerate electron liquids at metallic and lower densities, which accurately reproduces the Monte–Carlo results as well as those of the microscopic correlations and which satisfies the self–consistency condition in the compressibility sum rule and short range correction. The fitting formula is

\[ f_{IU}(q) = AQ^4 + BQ^2 + C + \left[ AQ^4 + \left( B + \frac{3A}{8} \right) Q^2 - C \right] \frac{4 - Q^2}{4Q} \ln \left[ \frac{2 + Q}{2 - Q} \right]. \]  

(2.42)

On the basis of IU [2.16] function, Farid et al (F) [2.18] have given a local–field correction that is of the form

\[ f_{F}(q) = AQ^4 + BQ^2 + C + \left[ AQ^4 + DQ^2 - C \right] \frac{4 - Q^2}{4Q} \ln \left[ \frac{2 + Q}{2 - Q} \right]. \]  

(2.43)

Recently, Sarkar et al (S) [2.17] proposed a simple form of local–field correction function, which is of the form

\[ f_{SS}(q) = A \left( 1 - \left( 1 + BQ^4 \right) \exp \left( -CQ^4 \right) \right). \]  

(2.44)
In expressions (2.42) to (2.44), \( Q = q / k_F \). The parameters A, B, C and D appearing in these expressions are well defined in the respective articles \([2.16 - 2.18]\). The natures of these \( f(q) \)s are plotted in Figure 2.1 and the dielectric function \( \varepsilon(q) \)s are shown in Figure 2.2.

![Plot of various local field correction functions \( f(q) \)](image_url)

**Figure 2.1: Plot of various local field correction functions \( f(q) \)**

It is seen from Figure 2.1 that local-field correction due to IU \([2.16]\) and F\([2.18]\) are showing peak at around \( q = 1.94k_F \). These \( f(q) \)s are involving the logarithmic singularity at \( q = 2k_F \). All these functions approaches to zero as \( q \to 0 \). At \( q \to \infty \) the limiting behavior is given as:

- \( f(q) \to \infty \) \quad For T\([2.15]\) and F\([2.18]\)
- \( f(q) \to 1 - g(0) \) \quad For IU \quad \( [2.24] \).
- \( f(q) \to C \) \quad For SS \quad \( [2.17] \)

From the Figure 2.2, it is observed that the inclusion of various local-field correction to the dielectric function \( \varepsilon(q) \), suppresses the static Hartree (H) \([2.2]\) dielectric function in the entire range of wave vector \( q \).
\[ W(q-q_0) = \frac{W_B(q)}{\varepsilon(q)} = 0. \] 

(2.45)

Figure 2.2: Plot of modified dielectric functions \( \varepsilon(q) \)

Model Potential

Pseudopotential is computed either through direct method or empirical method. But the usefulness of any potential depends upon how many number of parameters involves. The potential involving less number of parameters are considered the best one to avoid more complexities. Up till now we have seen that to construct the local potential one must cover

- The bare-ion local potential by which the electrons interacts with the ions.
- Hartree screening to take account of Coulomb interactions with the other conduction electrons.
- Effect of exchange and correlation.
The local Model pseudopotential depends on the ion positions only and hence they are generally used for the simplicity in the computations for the investigation of the properties of the matter.

From the beginning, the pseudopotential theory in its different forms (local, non-local, first principles) has done tremendous job in giving the understanding of large number of static and dynamic properties of simple metals over the last five decades. However, the applicability of local model pseudopotential to metallic complexes is a long-standing problem and it still remains a problem of interest in the field of condensed matter theory, materials science and engineering. Since last five decades, some single, double and multi-parametric pseudopotentials are developed for the calculation of the various properties of metals, liquid metals, semiconductors, alloys and glasses [2.19–2.58]. But it is found that most of these studies are scattered in the sense that so constructed pseudopotentials have not been consistently exploited for the comprehensive studies of atomic, dynamic, static, vibrational, electronic and magnetic properties. In the scattered studies, different authors have used different phenomenology and hence different forms in real-space with relevant parameters determined differently. The local-field corrections in the dielectric function have been used with different approximate expressions.

Looking to this situation, in the present work two kinds of model potentials are used for computing different physical properties of matter in different phases. The first one is the local model potential proposed by Ashcroft [2.44]. This potential is also known as empty core model potential. This potential is one of the fundamental and highly popular and consequently large numbers of studies are reported on the matter using this potential. The potential is as follows

**Ashcroft’s potential** : In real space:

\[
W_e (r) = \begin{cases} 
0 & ; r \leq r_c \\
-\frac{Ze^2}{r} & ; r > r_c 
\end{cases} 
\]  

This potential is known as the empty core model because the potential is zero inside the core. It is having Coulomb nature outside the core and the potential is continuous at the core radius \( r = r_c \). The Fourier transform of this potential gives us the potential in reciprocal space having the form (in Rydberg units), in momentum space:
Modified Ashcroft's potential:

The above Ashcroft's potential is modified for to incorporate the proper electron-ion interactions, this potential is well established [2.54-2.58]. The form of model potential in real space is

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

(2.48)

This model potential is continuous in \( r \)-space and it is the modified version of the Ashcroft's empty core model [2.44]. In comparison with Ashcroft empty core model potential, we have introduced \( \frac{Ze^2}{r} \exp \left(-\frac{r}{r_c}\right) \) as a repulsive part outside the core which vanishes faster than only Coulomb potential \( \frac{Ze^2}{r} \) as \( r \to \infty \). The corresponding form factor in the reciprocal space is

\[ W(q) = \left(\frac{4\pi Ze^2}{\Omega q^2}\right) \cos(qr_c) - \left\{ \frac{(qr_c) \exp(-1)}{1 + q^2 r_c^2} \right\} \left\{ \sin(qr_c) + (qr_c) \cos(qr_c) \right\} \]

(2.49)

Here, \( Z, e, \Omega, q \) and \( r_c \) are the valency, electronic charge, atomic volume, wave vector and the parameter of the potential, respectively. In the present investigations, the parameter of the potential is determined by employing values of the wave vector, \( q_0 \), where the form factor takes first zero value [2.6, 2.10, 2.14, 2.54-2.58], i.e. \( W_{\beta}(q) = 0 \) for \( q = q_0 \). For the present model potential, the condition is \( q_0 r_c = 1.343927 \) [2.54-2.58].

This leads to the condition for determining parameter of the potential as

\[ r_c = \frac{1.343927}{\frac{q_0}{2k_F}}. \]

(2.50)
After evaluation of the parameter of the potential the computation of the form factor becomes straightforward. Figure 2.3 and 2.4 shows the real-space nature of the potentials for lithium, sodium, Magnesium and aluminum, while Figure 2.5 and 2.6 shows the screened form factors in q-space for the same. As the screening has the same effect on the form-factor we have shown here the form-factor with Hartree [2.2] function only.

Table 2.1: Input data and potential parameter for model potential and Ashcroft’s potential

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>$K_F$ (au)$^{-1}$</th>
<th>$q/2K_F$</th>
<th>$\eta$</th>
<th>$\rho$ (gm/cm$^3$)</th>
<th>$r_c$ (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1</td>
<td>0.5890</td>
<td>1.13</td>
<td>0.46</td>
<td>0.504</td>
<td>1.17973</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.00976</td>
</tr>
<tr>
<td>Na</td>
<td>1</td>
<td>0.4882</td>
<td>0.98</td>
<td>0.46</td>
<td>0.928</td>
<td>1.64140</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.40459</td>
</tr>
<tr>
<td>Mg</td>
<td>2</td>
<td>0.7242</td>
<td>0.83</td>
<td>0.46</td>
<td>1.545</td>
<td>1.30661</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>1.16539</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td>0.9276</td>
<td>0.76</td>
<td>0.45</td>
<td>2.370</td>
<td>1.11405</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.99739</td>
</tr>
</tbody>
</table>

Figure 2.3: Model potential and Ashcroft’s potential for Lithium and Sodium in $r$-space
Figure 2.4: Model potential and Ashcroft’s potential for Magnesium and Aluminum in $r$-space

Figure 2.5: Form-factor of potentials for Lithium and Sodium
Figure 2.6: Form-factor of potentials for Magnesium and Aluminum

From the Figures following points are inferred:

The form factors generates limiting values $W(q) \rightarrow (-2/3)E_F$ as $q \rightarrow 0$ and $W(q) \rightarrow 0$ as $q \rightarrow \infty$. The highest $W_{\text{max}}(q)$ reaches beyond $q = q_0$ value. The form factors are free from any abnormal and unwanted oscillation. Proper convergence arises for higher wave vector $q$.

The present thesis is aimed to carryout theoretical investigation of various properties of elements, compound and alloy systems. The complete miscibility in the one element into another is rather considered as a rare case. Therefore, in such alloys the atomic matrix elements in the pure state are affected by characteristic of alloys such as lattice distortion effects and charging effects. For the investigation of various properties of $A_{1-x}B_x$ binary systems the input parameters and constants needed are determined using following relations:

$$
  r_c = (1-x) \, r_c(A) + x \, r_c(B)
$$

$$
  Z = (1-x) \, Z(A) + x \, Z(B)
$$

$$
  \Omega_0 = (1-x) \, \Omega_0(A) + x \, \Omega_0(B) \quad (2.51)
$$

Mitesh Joshi  
Sardar Patel University  
January (2010)
\[ M = (1-x) M_A + x M_B \]
\[ k_F = (1-x) k_F(A) + x k_F(B) \]

The subscript in parenthesis A and B in above expressions represents the pure component, while \( x \) is the concentration of element B in the alloy \( A_{1-x}B_x \).

### 2.1.5 Concept of pair potential

In order to understand the structural, transport and vibrational and other properties of condensed systems on a microscopic level, knowledge of their atomic structures and dynamics on the basis of realistic interatomic forces is important. The electronic behaviour in more than one component system (for liquid alloys and glasses) is inevitably much more complex than in one component system (liquid metals). For example, compound formation and charge transfer are not very well understood but are nevertheless, important effects which have to be taken into consideration. However, the nearly free electron model (NFE) [2.14] seems to be quite adequate for metallic binaries. Many qualitative and quantitative theories have been proposed to predict the properties of liquid alloys and mixtures, from knowledge of the pure components. The role of conduction electrons in liquid metals and alloys is particularly important in describing the properties with a more accurate knowledge of the interatomic force are necessary.

The pair potential is given by

\[
V(r) = \frac{Z^2 e^2}{r} + \frac{\Omega_0}{\pi^2} \int F(q) \frac{\sin qr}{qr} dq
\]

(2.52)

Here \( F(q) \) is the energy–wave number characteristics describe the indirect ion-electron–ion interactions in the wave number space and is written as [2.59-2.63],

\[
F(q) = -\frac{\Omega_0 q^2}{8\pi e^2} \left| V_B(q) \right|^2 \frac{[\epsilon_H(q) - 1]}{1 + [\epsilon_H(q) - 1][1 - f(q)]}
\]

(2.53)

In equation (2.53), \( \epsilon_H(q) \) is the Hartree dielectric function and \( f(q) \) is the local field correction function, which cares about the exchange and correlation effects and \( V_B(q) \) is the bare ion pseudopotentials.
Here the pair potential for liquid lithium and sodium is shown in figure 2.5 using model potential with the different screening functions as described earlier. The binary form of the pair potential is also described in the figure 2.6 for Sodium-Lithium alloy for specific concentrations (viz. Li$_{0.5}$Na$_{0.5}$ and Li$_{0.61}$Na$_{0.39}$).

Different screening functions as described earlier are employed for calculation of the pair-potentials for binary lithium-sodium alloy using model potential. This binary form of
the pair potential of lightweight Sodium-Lithium alloys with specific concentrations \( \text{Li}_0.5\text{Na}_0.5 \) and \( \text{Li}_0.61\text{Na}_0.39 \) are important nowadays, since the former is equi-concentrate alloy while the later is famed for having specific characteristics known as "zero alloy". More on these alloys will be discussed in the later chapters as when specific properties of these alloys are discussed.

### 2.2 The Density Functional theory

#### 2.2.1 Introduction

Density functional theory (DFT) is one of the most popular and successful quantum mechanical approaches to matter. It owes the versatility due to the generality of its fundamental concepts and the flexibility one has in implementing them. In spite of this flexibility and generality, it is based on quite a rigid 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 [2.67 - 2.70]. 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 a particular phenomenon on the atomic number \( Z \). And as we have discussed the electronic properties of solids and liquids are results of the behavior of the outer shell of valence and/or conduction electrons [2.71].

The DFT problem is non-trivial. Over the years many different methods and approaches have been proposed and used, all with different strengths and weaknesses. 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 timescale reflects the large investment in time required to develop computational programmes/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 problems that were completely out of reach just a few years ago [2.66].

Although the original papers on DFT provide an overview of the method, many of the improvements incorporated in different publications [2.64-2.100] 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 describes the quantum theory of materials with the special emphasize on DFT.

2.2.2 Basic Theory

The starting point of a quantum theory of materials is the Hamiltonian of the many ion many electron system. 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 the 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 a 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 \( R_i \) and the interaction of the electrons with each other electron.

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 problem 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 wavefunction by an antisymmetrized product of one-electron wavefunctions 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. [2.72-2.73]
On the other hand, the DFT, it is based on the famous theorem by Hohenberg and Kohn [2.74] 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 [2.75], where the exchange-correlation potential has been expressed as the functional derivative of the exchange-correlation energy. Where the only problem is that the functional is unknown. As a result, the core elements of DFT are the Hohenberg-Kohn theorem and the Kohn-Sham equations. In quantum mechanics all information about any system can possibly 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

\[
\left[ -\frac{\hbar^2 \nabla^2}{2m} + v(r) \right] \Psi(r) = E \Psi(r)
\]  

(2.54)

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

\[
\sum_i^N \left[ -\frac{\hbar^2 \nabla_i^2}{2m} + v(r_i) \right] + \sum_{i<j} U(r_i, r_j) \Psi(r_1, r_2, \ldots, r_N) = E \Psi(r_1, r_2, \ldots, r_N)
\]  

(2.55)

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

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

(2.56)

Note that this is the same operator for any system of particles interacting via the Coulomb interaction, just as the kinetic energy operator.
\[ \hat{T} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 \]  

(2.57)

is the same for any non-relativistic system. Whether our system is an atom, a molecule, or a solid thus depends only on the potential \( V(r_i) \). For an atom, e.g.,

\[ \hat{V} = \sum_i V(r_i) = \sum_i \frac{Qq}{|r_i - R|} \]  

(2.58)

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

\[ \hat{V} = \sum_i V(r_i) = \sum_i \frac{Q_k q}{|r_i - R_k|} \]  

(2.59)

Where 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 spatial 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 expression (2.56) differs from the extremely complex many-body problem. These properties are built into DFT in a very fundamental way. The usual quantum-mechanical approach to Schrödinger’s equation (SE) can be summarized by the following sequence

\[
V(r) \Rightarrow \Psi(r_1, r_2, r_3, \ldots, r_N) \Rightarrow \langle \Psi | \text{observable} | \Psi \rangle
\]  

(2.60)

i.e., one specifies the system by choosing \( V(r) \), plugs it into Schrödinger’s equation, solves that equation for the wave function, and then calculates observables by taking expectation values of operators with this wave function. One among the observables that are calculated in this way is the particle density.

\[
n(r) = N \int d^3 r_2 \int d^3 r_3 \ldots \int d^3 r_N \Psi^*(r, r_2, \ldots, r_N) \Psi(r, r_2, \ldots, r_N) \]  

(2.61)
2.2.3 The Hohenberg-Kohn theorem

In the Hohenberg-Kohn equation the system of N interacting (spinless) 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 [2.74] demonstrated the opposite, far less obvious result 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 ad absurdum argument.

Let us consider a many-electron Hamiltonian $H = T + U + V$, with ground state wavefunction $\Psi$. $T$ is the kinetic energy, $U$ the electron-electron interaction, $V$ the external potential. The charge density $n(r)$ is defined as

$$n(r) = N \int \left| \Psi(r_1, r_2, ..., r_N) \right|^2 dr_1 ... dr_N$$  \hspace{1cm} (2.65)

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

$$E' = \langle \Psi' | H' | \Psi' \rangle = \langle \Psi | H | \Psi \rangle = \langle \Psi | H + V' - V | \Psi \rangle$$  \hspace{1cm} (2.66)

That is,

$$E' < E + \int (V(r) - V'(r)) n(r) dr$$  \hspace{1cm} (2.67)

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. 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,

$$E[n(r)]=\langle \Psi | T + U + V | \Psi \rangle$$

$$=\langle \Psi | T + U | \Psi \rangle + \langle \Psi | V | \Psi \rangle$$

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

(2.68)

Where $F[n(r)]$ is a universal functional of charge density $n(r)$ and not $V(r)$. Furthermore, the minimum value of $E$ is $E_0$, 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 with 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 [2.75] that this functional could be written

$$F[n(r)]=T_s[n(r)] + \frac{e^2}{2} \int \frac{n(r)n(r')}{|r - r'|} d^3r d^3r' + E_{xc}[n(r)]$$

(2.69)

Here 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 the 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 wavefunctions $\{ \psi_i \}$ such that

$$n(r) = \sum_i |\psi_i(r)|^2$$

(2.70)

The kinetic energy term may be written

$$T_s[n(r)] = \sum_i -\frac{\hbar^2}{2m_e} \int \psi_i^* \nabla^2 \psi_i d^3r$$

(2.71)
Minimizing $E[n(r)]$ with respect to $n(r)$ subject to the constraint that the number of electrons must be constant, leads us to a set of equations for each $i$,

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(r)\right)\psi_i(r) = \epsilon_i \psi_i(r) \quad (2.72)$$

Where $V_{\text{eff}}$ is an 'effective potential',

$$V_{\text{eff}} = V_{\text{ext}}(r) + \int \frac{e^2 n(r')}{|r-r'|} d^3r' + V_{XC}(r) \quad (2.73)$$

and $V_{XC}(r)$ is the exchange-correlation potential $\frac{\delta E_{XC}}{\delta n(r)}$. Equation can be seen to be a set of Schrödinger-like equations for the single particle Kohn-Sham orbitals

$$\hat{H}_{\text{KS}} |\psi_i\rangle = \epsilon_i |\psi_i\rangle \quad (2.74)$$

Thus, the problem of a system of interacting electrons has been mapped onto a system of non-interacting electrons moving in an effective potential given by Equation. 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 [2.76-2.80]. The construction of suitable basis functions is a major enterprise within electronic-structure theory (DFT), and the following lines do little more than explaining some acronyms often used in this field.

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, in that they are centered on atoms, but functions centered in bonds or lone pairs, and pairs of functions centered in the two lobes of a single orbital, have been used. 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.

### 2.2.4 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 orbitals (LCAOs); (ii) linearized augmented plane waves (LAPWs); or (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 wavefunctions and potential are atomic-like (i.e. almost spherical-symmetric and strongly varying with radial distance), while in the interstitial regions potential and wavefunctions 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 (Pisani et al. [2.81]) and have recently enjoyed renewed popularity [2.82, 2.83].

In the LAPW approach space is divided into spheres centered around 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 [2.84], 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 [2.85-2.86]. Similar basis sets are used also in the linear-muffin-tin-orbital (LMTO) [2.87-2.89] and Kohn-Korringa-Rostocker (KKR) [2.90] 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 [2.91]. 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) convergence 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) forces 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 [2.92]. The drawback is that in order to achieve convergence with a manageable size of the basis set, the strong electron-ion interaction must be replaced by a sufficiently weak pseudopotential. The basic idea of the pseudopotential approach is to project the Schrödinger equation for the valence electrons onto the subspace orthogonal to the core orbitals [2.6, 2.93 - 2.94], eliminating the nodal structure of the valence orbitals close to the core without modifying them in the region where chemical bonding occurs. Much effort has been spent in constructing pseudopotentials 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 [2.95-2.100], but the difficult cases are the first-row elements and the transition and rare-earth elements with node-less 2p, 3d and 4f orbitals where the usual concepts fail. For these elements the so-called ultra-soft pseudopotentials (US-PP) supplementing a PW representation of the smooth part of wavefunctions, charge densities and potentials with localized augmentation functions are by far the most efficient solution [2.100-2.101].

One of the main advantages of 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 localised 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 [2.95-2.101], in conjunction with plane waves, can dramatically reduce the magnitude of this problem. To understand what pseudopotentials 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 sit tightly bound to their host nuclei, and only the valence electrons are involved in chemical bonding. Therefore it is possible to incorporate the core states into a bulk nuclear potential, or pseudo-potential, and only deal with the valence electrons separately.

Core wavefunctions are rapidly varying with many nodes, and require a large number of fitting functions to model accurately; pseudopotentials overcome this as the pseudo-wavefunction is smoothly varying and node-less within a certain core radius. In addition the Coulombic interaction of core states would tend to swamp any total energy calculations trying to compare small differences in valence bond energies. In order to remain orthogonal to the core states, the valence 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 valence wavefunctions can be replaced with a smoothed form; beyond this radius the pseudo-wavefunction must be identical to the full all-electron wavefunction. In addition there will still be exchange interactions between core and valence 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' pseudo-potentials) [2.101-2.109].

![Pseudo-wavefunction](image)

**Figure 2.8: Pseudo-wavefunction**

(The 4s (full) and pseudo- (dashed) radial wavefunction (in atomic units) for the isolated Ni atom.)

Figure 2.8 shows the radial 4s full- and pseudo- wavefunction for Ni. It can be seen that the rapidly varying core region has been smoothed in the pseudo-wavefunction but beyond the cut-off radius ($r_c$), the pseudo- and all-electron- wavefunctions are identical.

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

1. Real and pseudo- valence eigenvalues agree for a chosen ``prototype'' atomic configuration.
2. Real and pseudo- atomic wave functions agree beyond $r_c$, chosen ``core radius''.
3. The integrals from 0 to $r$ of the real and pseudo charge densities agree for $r > r_c$ for each valence 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 is to bring to notice that the last two points are essential if the pseudopotential is to have optimum transferability.

### 2.2.5 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 valence, 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 behaviour of the valence electrons is not affected outside of 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 behaviour of condensed matter. By using pseudopotentials the computational cost of a calculation is reduced in three ways [2.109]:

- 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.

- Because there are no core-electrons to which valence 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.

- 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.
Because we only explicitly treat the valence 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.

### 2.2.6 Local Density Approximation (LDA)

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 in an homogeneous 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 [2.110] and used to construct exchange-correlation functionals within the framework of a local density approximation (LDA), the most widely used such functionals are due to von Barth and Hedin [2.111], Perdew and Zunger [2.112], and Vosko et al. [2.113]. 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 [2.111]. 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 [2.114].

The LDA is generally very successful in predicting structures and macroscopic properties, but some shortcomings are notorious as well. These concern in particular: (i) 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 appropriately described in the LDA, although there are some recent suggestions for overcoming this problem [2.115-2.117].
2.2.7 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 Perdew and co-workers [2.118, 2.120-2.122] 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 larger lattice constants and lower cohesive energies) [2.123-2.124] 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 functionals available are listed below in table.

<table>
<thead>
<tr>
<th>Functional</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirac-Slater [2.110]</td>
<td>LDA</td>
</tr>
<tr>
<td>Von Barth-Hedin [2.111]</td>
<td>LDA</td>
</tr>
<tr>
<td>Becke [2.128]</td>
<td>GGA</td>
</tr>
<tr>
<td>Perdew-Wang [2.121]</td>
<td>GGA</td>
</tr>
<tr>
<td>Perdew-Burke-Ernzerhof [2.122]</td>
<td>GGA</td>
</tr>
</tbody>
</table>

Table 2.2 : List of exchange and Correlation functional
(b) Correlation

<table>
<thead>
<tr>
<th>Functional</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perdew-Zunger [2.112]</td>
<td>LDA</td>
</tr>
<tr>
<td>Von Barth-Hedin [2.111]</td>
<td>LDA</td>
</tr>
<tr>
<td>Perdew-Wang [2.121]</td>
<td>LDA</td>
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<tr>
<td>Vosko-Wilk-Nusair [2.113]</td>
<td>LDA</td>
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<tr>
<td>Perdew [2.118]</td>
<td>GGA</td>
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<tr>
<td>Lee-Yang-Parr [2.129]</td>
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<td>Perdew-Wang [2.121]</td>
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<tr>
<td>Perdew-Burke-Ernzerhof [2.122]</td>
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</table>

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

1. The initial guess of the density $n(r)$
2. Computation of the potential using
   
   \[ V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int d^3 r \cdot \frac{e^2 n(r)}{r - r} + V_{\text{xc}}(n(r)) \]

3. Find the $N$ lowest eigenvalues of Schrödinger equations
   
   \[ E_n \psi_n = -\frac{\hbar^2}{2m} \nabla^2 \psi_n + V_{\text{eff}} \psi_n \]

4. Get the density from the wave function
   
   \[ n(r) = \sum_{i=1}^{N} \psi_n^*(r) \psi_n(r) \]

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

The general flow chart of above procedure can be given by
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 [2.127] and VASP [2.123] code for the said purpose.
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Chapter 2

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