# Pseudopotential and Screening Theory

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Theory of pseudopotential.</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>Theory of screening.</td>
<td>21</td>
</tr>
<tr>
<td>2.3</td>
<td>Pseudopotential Form factors.</td>
<td>25</td>
</tr>
</tbody>
</table>
2.1 THEORY OF PSEUDOPOTENTIAL:

In principle, we should be able to find out everything about a crystal by solving Schrödinger equation for a system of interacting nuclei and electrons that form the crystal. The pseudopotential method is a technique for solving the Schrödinger equation for the energy of the conduction electrons. This problem, however is very complicated as well as difficult to solve and therefore it is necessary to look for certain simplifications for making the problem meaningful and manageable. A crystal is visualized as made up of light particles (electrons) and heavy particles (nuclei). Since the electrons of the inner atomic shells do not take part in any electro-physical processes in the crystal we can divide the system into two distinct regions: (i) The region consisting of the nuclei and the electrons in the completely filled shells which is termed as the "core region". (ii) The region outside the core consisting of the valence electrons, which are responsible for the atomic binding.

The stationary state of the particles is described by the solution of Schrödinger equation:

\[ H_T \Psi_T = E_T \Psi_T, \]  \hspace{1cm} (2.1)

where \( H_T \) is the total crystal Hamiltonian, \( \Psi_T \) is its wave function and \( E_T \) its eigen value, or the crystal energy. The Hamiltonian \( H_T \) includes:

(1) The kinetic energy of electrons,

\[ T_e = \sum_i T_i = \sum_i \frac{-\hbar^2 \nabla_i^2}{2m_e}, \]  \hspace{1cm} \ldots (2.2)

\( m_e \) is the electron mass.

(2) The electron-electron interaction energy,

\[ U_e = \frac{1}{2} \sum_{ij \neq 1} \frac{e^2}{|r_i - r_j|} = \frac{1}{2} \sum_i U_{ij}, \]  \hspace{1cm} \ldots (2.3)

\( r_i \) and \( r_j \) denote the electron coordinates and \( e \) the electronic charge.

(3) The energy of electron-ion interaction,

\[ U_{ei} = \sum_i \sum_{\alpha} \frac{Z_{\alpha} e^2}{|r_i - R_{\alpha}|} = \sum_i U_{i\alpha}, \]  \hspace{1cm} \ldots (2.4)

\( R_\alpha \) denotes the ionic coordinates and \( Z_\alpha \) the ionic charges.

(4) The kinetic energy of the ions,

\[ T_i = \sum_{\alpha} \frac{-\hbar^2 \nabla_{\alpha}^2}{2m_\alpha}, \]  \hspace{1cm} \ldots (2.5)
\( m_\alpha \) is the ionic mass.

(5) The energy of ion - ion interaction,

\[
U_i = \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta e^2}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|},
\]

... (2.6)

\( Z_\alpha \) and \( Z_\beta \) are the ionic valances.

(6) The energy of all the particles in an external field,

\[
V = V(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3, \ldots)
\]

... (2.7)

Thus the total Hamiltonian may be written as

\[
H_{\text{tot}} = T_e + T_i^+ U_i + U_e + U_{\text{ex}} + V.
\]

... (2.8)

Electrons are Fermions (the wave function must be antisymmetric for interchange of any two electrons), while nuclei are Fermions, Bosons or distinct particles according to the particular situation under examination. The only stabilizing terms in the Hamiltonian is the interaction between electrons and nuclei, all other terms are repulsive. The total Hamiltonian for the system can be written as, neglecting external interactions,

\[
H_T = H_i + H_e,
\]

... (2.9)
where

\[ H_1 = T_1 + U_1 , \]

\[ H_e = T_e + U_e + U_{el} . \]

All the ingredients entering the Hamiltonian are perfectly known and all the properties can be derived by solving the Schrödinger equation. But a number of approximations are necessary before this can be achieved in practice. The Schrödinger equation (2.1) is very hard to solve exactly so we introduce the adiabatic approximation to simplify the problem. The adiabatic approximation or the Born - Oppenheimer approximation, takes account of the difference in motion of electrons ( light particles ) and ions ( heavy particles ). The massive ions do not follow the rapidly changing spatial distribution of all the electrons but moves in the averaged field of all the electrons. At the same time the ion moving relatively slowly is accompanied by the electrons, and the atom thus remains intact ( the atoms in the materials preserve their identity). Therefore a rough assumption is that the ions remain stationary. This helps us to uncouple the electron part of the equation from the ion part. The root of the adiabatic approximation is that the typical excitation energy for the nuclei (\( \hbar \omega_{nuc} \sim 10 \text{ meV} \)) is a few order of magnitude smaller than the one for electronic excitations (\( \hbar \omega_{ele} \sim 1 \text{ eV} \) ); So, on the time scale electrons need to readjust themselves, ions essentially don’t move. Assuming that the ions are frozen in time during the motion of the electrons the full wave function \( \Psi_T \) can be broken up as follows:

\[ \Psi_T = \Psi_1 + \Psi_e . \]
This is yet not an approximation. The approximation is in the assumption that the electronic motion does not depend on the velocity of the nuclei but only on their positions. In the adiabatic approximation the kinetic energy of the ions turns out to be zero and with proper choice of reference energy the interaction energy of ions which becomes a constant can be made zero [1,10]. The conduction electron energy then becomes an effective potential energy of the ions [46]. Thus as a result of the adiabatic approximation the electron wave function should satisfy the equation

$$H_e \Psi_e = E_e \Psi_e \quad \ldots (2.12)$$

or

$$\left[ -\frac{\hbar^2}{2m_i} \nabla_i^2 + \frac{1}{2} \sum_{ij} U_{ij} + \sum_{i\alpha} U_{i\alpha} \right] \Psi_e = E_e \Psi_e \quad \ldots (2.13)$$

Even after introducing the adiabatic approximation, the problem of solving the Many-Body Schrödinger equation for the electrons at fixed atomic positions is extremely difficult. This equation also can not be solved exactly. It has to be transformed into an equation for one particle, which is called one-electron approximation. The motion of any given electron depends on the motion of all other electrons, but since it itself affects the motion of other electrons, the motion of all electrons is self-consistent. This fact makes it possible to introduce the quantity $V(r)$ - the energy of the electron in the field of all the electrons which takes into account the effect of the former on their motion. This potential $V(r)$ is termed self-
consistent[2]. The introduction of the self-consistent field enables the problem of a system of interacting particles to be reduced to a one-particle problem.

In the one-electron approximation we may represent the Hamiltonian of an arbitrary electron in the form

$$H = \frac{-\hbar^2 V_i^2}{2m} + V(r) = T_e + V(r). \quad \ldots (2.14)$$

The energy $E$ of the electron and its wave function may be found from the equation

$$\left[ \frac{-\hbar^2 V_i^2}{2m} + V(r) \right] \Psi = E \Psi. \quad \ldots (2.15)$$

The pseudopotential method for evaluating the electron-ion-electron interaction follows the technique of orthogonalised plane wave (OPW) in which the conduction electron wave functions are orthogonal to any core states. The orthogonality of the conduction electrons is expressed by

$$<\Psi_k | \Psi_{k'}> = \delta_{kk'}. \quad \ldots (2.16)$$
The electrons in the ion cores are denoted by the index $\alpha$, where $\alpha$ enumerates all the core electrons in all the ions, and a single core-electron wave function is represented by $|\alpha>$. According to Herring [47] $\Psi_k$ must be orthogonal to the $|\alpha>$, that is,

$$<\alpha|\Psi_k> = 0,$$  \hspace{1cm} (2.17)

and this can be ensured by writing $\Psi_k$ in the form

$$\Psi_k = (1 - P) \Phi_k,$$ \hspace{1cm} (2.18)

where $P = \sum_a |\alpha><\alpha|$ \hspace{1cm} (2.19)

is the projection operator.

It should be noted that since $\Psi_k$ is orthogonal to $|\alpha>$, then according to equation (2.16) $\Phi_k$ can not be orthogonal. We can now write pseudo-wave functions and the correct conduction electron energies $E_k$. From equations (2.15) and (2.18) we can write

$$H (1 - P) \Phi_k = E_k (1 - P) \Phi_k,$$ \hspace{1cm} (2.20)

$$[H (1 - P) + E_k] \Phi_k = E_k \Phi_k.$$ \hspace{1cm} (2.21)

So,

$$T_e (1 - P) \Phi_k + V(r) (1 - P) \Phi_k + E_k P \Phi_k = E_k \Phi_k.$$ \hspace{1cm} (2.22)

Rearranging the terms in the above equation, we get
\[ T_e \Phi_k + V(r) \Phi_k - [ T_e + V(r) ] P \Phi_k + E_k P \Phi_k = E_k \Phi_k . \quad \ldots (2.23) \]

Therefore

\[ T_e \Phi_k + W \Phi_k = E_k \Phi_k , \quad \ldots (2.24) \]

where

\[ W = V(r) - [ T_e + V(r) ] P + E_k P . \quad \ldots (2.25) \]

or

\[ W = V(r) + [ E_k - ( T_e + V(r) ) ] P = V(r) + \sum [ E_k - E_\alpha ] |\alpha > < \alpha | \quad \ldots (2.26) \]

\[ = \text{the pseudopotential operator} \]

The contribution to W in the region outside the ion cores V(r) which is comprised of Coulomb potentials arising from the ions and from other electrons. Inside the ion cores V(r) is large and negative, due to the unscreened nuclear charge while [ E_k - ( T_e + V(r) ) ] P is large and positive because [ T_e + V(r) ] operates on P to produce core electron energies E_k and the band electron energies E_k lie well above the core energies. While W\Phi_k has to be small compared to T_e \Phi_k \ [6,7]. Hence the net effective potential inside the core is small and is known as the pseudopotential. This weak pseudopotential W, can be treated as a perturbation.
In the general equation of the pseudopotential the term $V(r)$ contains the potential due to the cores, which may be written as a sum of potentials associated with the individual ions at positions $r_j$ which are spherically symmetric.

$$V_i(r) = \sum_j v_i(r - r_j) \ldots (2.27)$$

The pseudopotential may be written as a sum of contribution from individual ion sites as

$$W(r) = \sum_{ij} w(|r_i - R_j|), \ldots (2.28)$$

where $r_i$ and $R_j$ refer to the electronic and ionic coordinates respectively. Due to the weak strength of the potential $W(r)$, the matrix element $\langle k+q | W | k \rangle$ can be written using perturbation expansion as,

$$\langle k+q | W | k \rangle = S(q) \langle k+q | W | k \rangle \ldots (2.29)$$

with

$$S(q) = \frac{1}{N} \sum_j \exp(-i\mathbf{q} \cdot \mathbf{r}) \ldots (2.30)$$

$$= \text{structure factor}$$

and

\begin{equation}
\langle k+q \mid W \mid k \rangle = \frac{1}{\Omega_0} \int_{\Omega_0} \exp \left[ -i (k + q) \cdot r \right] W(r) \exp \left[ i q \cdot r \right] d^3 r \ldots (2.31)
\end{equation}

\textit{form factor}

where \( \Omega_0 = \Omega / N = \) atomic volume.

The \textit{structure factor} \( S(q) \) gives the measure of correlation between position of atoms and depends only upon the ion positions \( R_j \). The \textit{form factor} \( \langle k+q \mid W \mid k \rangle \) depends only upon the individual ion potentials and is independent of the ion positions. The factorization of the matrix element into structure factor and form factor helps us to investigate the properties of liquids and alloys more easily. The information about ionic potentials enter through the form factor while that of the ionic positions through the structure factor in the computations.

A pseudopotential \( W(r) \) is usually nonlocal as formfactor \( \langle k+q \mid W \mid k \rangle \) depends both on the vector difference \( q \) and the vector \( k \) itself. Nonlocality arises when the pseudopotential, unlike the original crystal potential is not a multiplication operator. A nonlocal form factor is extremely inconvenient to work with because for any given pair of \( k \) and \( q \) the functions that must be calculated are rather complicated. So people prefer to work with a local pseudopotential. An interesting freedom with the local pseudopotential is that it's form is not unique. Therefore quite a number of pseudopotentials are predicted for a particular system. While doing so, the important criterion is that it must lead to the same overall picture.
2.2 THEORY OF SCREENING:

When an atom is placed in a free electron gas, the electron density around it is changed. The total displaced charge is equal to the charge of the ion. i.e. the potential is screened by the electron gas. In a real crystal the electrons screening a potential are not free but we have to ignore this in the pseudopotential theory as, otherwise the problem of constructing a screened pseudopotential becomes very hard to solve. The dielectric screening plays a very important role in the evaluation of self-consistent potential due to the screening of the electron gas, and hence is fundamental for understanding the behaviour of metals. Thus an accurate understanding of the dielectric function of an electron gas is necessary for the investigation of the electron correlations. Harrison [2] has discussed this aspect in detail and we avoid here the same repetition. In this formulation the Hartree screening function turns out to be

\[
\left[ \varepsilon_h(q) - 1 \right] = \frac{me^2}{2\pi \hbar^2 k_F Y^2} \left[ 1 + \frac{(1-Y^2)}{2Y} \right] \ln \left| \frac{1+Y}{1-Y} \right| ; \ Y = q / 2 k_F . \quad (2.32)
\]

The total one electron potential \( W(r) \) may be written as [15]

\[
W(r) = W_B(r) + W_s(r) , \quad \ldots (2.33)
\]

\( W_B(r) \) represents the "bare" interaction. Electrons interact with each ion through this potential which includes the Coulomb potential of the ion. In addition, each electron interacts with the...
others through a Coulomb potential which can be determined from the charge density due to all electrons, that is, a self-consistent field represented here by $W_s(r)$. In q space the Hartree potential is given as

$$W_s(q) = W(q) \left[ 1 - \varepsilon_H(q) \right]. \quad (2.34)$$

As $W(q) = W_B(q) + W_s(q)$,

equation (2.34) can be solved for $W(q)$ in terms of $W_B(q)$ to find

$$W(q) = \frac{W_B(q)}{\varepsilon_H(q)}. \quad (2.36)$$

Thus $\varepsilon_H(q)$ plays the role of a static dielectric function. The screened potential can be obtained from the unscreened potential simply by division by $\varepsilon_H(q)$. This method was first used by Cohen and Phillips [48]. As the function $\varepsilon_H(q)$ depends only upon the magnitude of $q$ the screened potential is spherically symmetric just like the unscreened potential. The function $\varepsilon_H(q)$ as defined above does not take into account the exchange and correlation effects. Now we include the exchange and correlation effects in a local one electron potential $W_x(q)$, so that

$$W(q) = W_B(q) + W_s(q) + W_x(q) \quad (2.37)$$

$$= W_B(q) + W_{sx}(q). \quad (2.38)$$
The exchange potential is related to the Hartree potential [2] by,

$$ W_{sx}(q) = W_s(q) \left[ 1 - f(q) \right], \quad \ldots (2.39) $$

where $f(q)$ is represented by an interpolation approximation. Combining equations (2.34) and (2.39) leads to,

$$ W_{sx}(q) = W(q) \left[ 1 - e_H(q) \right] \left[ 1 - f(q) \right]. \quad \ldots (2.40) $$

Solving for $W(q)$ in terms of $W_B(q)$ gives

$$ W(q) = \frac{W_B(q)}{\{1 + \left[ 1 - e_H(q) \right] \left[ 1 - f(q) \right]\}} = \frac{W_B(q)}{\varepsilon(q)} \quad \ldots (2.41) $$

Here

$$ \varepsilon(q) = \{1 + \left[ 1 - e_H(q) \right] \left[ 1 - f(q) \right]\}, \quad \ldots (2.42) $$

is the modified dielectric function [15]. The function $f(q)$ incorporates the exchange and correlation effects in the screening function and is called the local field correction function.

After Fourier transformation, small $q$ corresponds to large $r$, i.e. screening renormalises the long range nature of the Coulomb potential. Therefore screening is important at small $q$. A pure unscreened Coulomb potential always produces bound states and the perturbation expansion will therefore be always divergent. This may be avoided by assuming “background”
screening leading to a short-range potential. Depending on the “strength” of the initial model potential the screened pseudopotential acquires a repulsive region either inside the well or outside it. A correct description of the dielectric screening function, hence plays a vital role in the study of solids, liquids and alloys. Various expressions for “f(q)” used by different investigators as found in the literature survey [49-64] are listed in Table 2.1.

Table 2.1: Various forms of the local-field correction function f(q).

<table>
<thead>
<tr>
<th>Reference</th>
<th>f(q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hartree (RPA) [48]</td>
<td>0</td>
</tr>
<tr>
<td>2. Harrison [48]</td>
<td>(1/2 \left[ \frac{q^2}{q^2 + 4k_F^2/3} \right])</td>
</tr>
<tr>
<td>3. Hubbard - Sham [49,50]</td>
<td>(q^2 / \left[ 2 \left( q^2 + \xi k_F^2 \right) \right] )</td>
</tr>
<tr>
<td>4. Shaw [51]</td>
<td>1 - exp((-2.14q^2))</td>
</tr>
<tr>
<td>5. Hubbard - Sham - Geldert - Vasko [52]</td>
<td>(q^2 / \left[ 2 \left( q^2 + \xi^2 \right) \right] )</td>
</tr>
<tr>
<td>6. Kleinman - Langreth [53,54]</td>
<td>(1/4 \left[ \frac{q^2}{q^2 + k_F^2 + k_s^2} \right] + \frac{q^2}{(k_s^2 + k_F^2)} ) ; (k_s^2 = 2k_F/\pi a_0)</td>
</tr>
<tr>
<td>7. Shaw - Pynn [55]</td>
<td>(1/2 \left[ 1 - \exp \left( q^2/\beta k_F^2 \right) \right] + \left( \frac{1/2 \left[ \exp \left( q^2/k_F^2\right) \right]}{1 + \exp \left( q^2/k_F^2\right) \right} \right) )</td>
</tr>
<tr>
<td>8. Singwi - Sjølnder - Tosi - Land [56]</td>
<td>(4A \left[ 1 - \exp \left( -Bq^2/k_F^2 \right) \right] )</td>
</tr>
<tr>
<td>9. Toigo - Woodruff [57]</td>
<td>Numerical Table</td>
</tr>
<tr>
<td>10. King - Cutler [58]</td>
<td>(q^2 / \left[ 2 \left( q^2 + 2k_F^2 \right) \right] )</td>
</tr>
<tr>
<td>11. Mahanti - Das [59]</td>
<td>(1/2 \left[ \left{ \frac{q^2}{k_F^2} \left( \xi^2 + 1 \right) \right} + \left{ \frac{q^2}{(q^2 + k_F^2)(\xi^2 + 1)} \right} \right] )</td>
</tr>
<tr>
<td>12. Overhauser [60]</td>
<td>0.275 (X^2 / \left[ 1 + 2.5X^2 + 0.09375X^4 \right]^{1/2} ; X = q/k_F )</td>
</tr>
<tr>
<td>13. Vashishta - Singwi [61]</td>
<td>(A \left[ 1 - \exp \left( -Bq^2/k_F^2 \right) \right] )</td>
</tr>
<tr>
<td>14. Srivastava [62]</td>
<td>(1/2 \left[ 1 - \exp \left( -q^2 / (q^2 + \xi k_F^2) \right) \right] )</td>
</tr>
<tr>
<td>15. Taylor [63]</td>
<td>(q^2 / 4k_F^2 \left( 1 + 0.1534 / \pi k_F \right) )</td>
</tr>
<tr>
<td>16. Ichimaru - Utsumi [64]</td>
<td>(A Q^4 + B Q^2 + C + \left[ A Q^4 + \left( B + 8A/3 \right) Q^2 - C \right] \times \left( \frac{4 - Q^4}{4Q} \right) \ln \left( \frac{2 + Q}{2 + Q} \right) )</td>
</tr>
</tbody>
</table>

with \(Q = q/k_F\).
2.3 PSEUDOPOTENTIAL FORM FACTORS:

The electron-ion interaction described by the pseudopotential form factor is the most important and fundamental ingredient in the study of condensed matter physics. The problem of establishing an effective electron-ion interaction in any metal, either from first principles or on a pseudopotential approach, has been of considerable interest during the last three decades. The detailed information of the bare-ion potential and a proper dielectric function is necessary for the determination of the fundamental properties at metallic densities.

The exact form of the pseudopotential is quite complicated which involves many-body effects (being nonlocal and eigen value dependent). People generally prefer to use the local approximation for describing the electron-ion interaction in metals. The evaluation of the effective electron-ion interaction in metals has been done by different methods including direct calculations [59,65], empirical methods [10,11,66] and model pseudopotentials formulations [2,12] in the past. This has also been done from first principles [67] using Hartree-Fock functions of the ions or obtained from experimental measurements. The use of the local approximation for describing various properties of simple and non transition metals have been reviewed by Harrison [2], Weaire [12], Brovman and Kagan [13] and also by Pickett [17].

It is found that the construction of a local pseudopotential must cover: (i) the bare-ion local potential by which the electrons interact with ions, (ii) Hartree screening to take into account only Coulomb interactions with other conduction electrons and (iii) the effect of exchange and correlation. The cardinal point in the formulation of a suitable local
pseudopotential is the proper assumption of $W^B(r)$, and it's Fourier transform which can lead to a well behaved form factor. Alternately one can also assume $W^B(q)$ directly in $q$-space for the calculation of various properties \[68-70\].

A common technique for the selection of a pseudopotential is to take a simple parametric form and fitting it to some experimental property. Local pseudopotentials with single parameter model proposed by Ashcroft \[71\], and two parameter model proposed Heine-Abrankov \[72\] are more frequently used in many pseudopotential based studies. It is evident that, if the number of parameters is increased, any conceivable data can be fitted with arbitrary precision. Also the pseudopotential fitted with one property needs a slight readjustment when applied to other property. This is because interactions important in determining one experimental result may not be important in another case. All pseudopotentials have their merits and demerits. Although not only the choice of the pseudopotential is important but the choice of the electron gas dielectric function is equally fundamental in any study.

Keeping this in mind we have proposed a single parametric local model pseudopotential which has the following form in real space.

$$W^B(r) = \begin{cases} 0 & ; r < r_c \\ \frac{Ze^2}{r} \left[ 1 - \exp\left(-r/r_c\right) \right] & ; r \geq r_c \end{cases} \quad \ldots (2.43)$$

where \( Z \) is the valence, \( e \) the charge of the electron and \( r_0 \) the parameter of the potential. This model potential is continuous in \( r \) space. The proposed model potential is the modified version of the Ashcroft's empty core model [71]. In this we have introduced some repulsive part outside the core which vanishes faster than only Coulomb potential \(-Ze^2/r\) as \( r \to \infty \).

Moreover, it may be noted that the inclusion of this repulsive term outside the core makes the effective core smaller than the ionic radius of a free ion. Hence, as a result this supports the small core approximation which is essential in the formulation of a pseudopotential. The Fourier transform of equations (2.43) leads to the expression for \( W^B(q) \) which is given by,

\[
W^B(q) = -\frac{8\pi Z}{\Omega_0 q^2} \left[ \cos(q r_c) - \frac{(q r_c) e^{-1}}{(1+q^2 r_c^2)} \{\sin(q r_c) + (q r_c) \cos(q r_c)\} \right]. \quad \ldots (2.44)
\]

This expression (2.44) is in rydberg units and \( e \) is the base of natural logarithm. This model potential gives the correct limiting values of \( W^B(q) \) [15], i.e.

\[
\lim_{q \to 0} W^B(q) = -\frac{8\pi Z}{\Omega_0 q^2} \quad \ldots (2.45)
\]

and

\[
\lim_{q \to \infty} W^B(q) = 0. \quad \ldots (2.46)
\]
To obtain the screened form factor from among the various forms of the local field correction functions $f(q)$ found in the literature survey [49-64] and listed in Table 2.1, we have selected the functions due to Hartree [2], Taylor [63] and Ichimaru and Utsumi [64] in the present study. Reasons for selecting these three functions is that Hartree function is the static dielectric function and does not include any exchange and correlation effects among the conduction electrons, while the Taylor [63] function covers the overall features of the various local field corrections functions proposed before 1972. The Ichimaru Utsumi [64] screening function is the recent one among all those listed in Table 2.1 and possesses various interesting properties.

The Hartree (H) local field function does not include the exchange and correlations effects and hence for that

$$f(q) = 0. \quad \text{...(2.47)}$$

The analytical expression for $f(q)$ introduced by Taylor (T) is given by

$$f(q) = \frac{q^2}{4 \, k_F^2} \left[ 1 + \frac{0.1534}{\frac{\pi \, k_F}{1}} \right]. \quad \text{...(2.48)}$$

This function satisfies the compressibility sum rule exactly. These two functions and some of the functions given in Table 2.1 are more commonly used in pseudopotential calculations. Out of these the function due to Geldart and Vosko [52] leads to a negative pair correlation
function, a physically incorrect result, while that of Kleinmann [53,54] gives a pair correlation function which is negative infinity, over the entire range of metallic densities.

It is found that the local field function of Ichimaru and Utsumi (IU) [64] has not been used extensively in the comprehensive study of metals, binary alloys and metallic glasses. This function 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 calculations and which satisfies the self-consistency conditions in the compressibility sum rule and the short range correlations.

This function was derived using (i) The Monte Carlo data of Ceperly and Alder [73] for the correlation energy, (ii) the ladder diagram calculations of short range calculations by Yasuhara [74], and (iii) the self consistent dielectric formulation of Utsumi and Ichimaru [64]. The fitting formula describing \( f(q) \) is given as,

\[
f(q) = AQ^4 + BQ^2 + C + \left[ AQ^4 + \frac{(B+3A/8)Q^2 - C}{4Q} \right] \ln \left| \frac{2 + Q}{2 - Q} \right| \quad \ldots (2.49)
\]

with \( Q = q / k_F \),

where

\[
A = 0.029 \quad (0 \leq r_s \leq 15) \quad \ldots (2.50)
\]
\[ B = \left( \frac{9}{16} \right) \gamma_0 - \left( \frac{3}{64} \right) [1 - g(0)] - \left( \frac{16}{15} \right) A \] ... (2.51)

\[ C = -\left( \frac{3}{4} \right) \gamma_0 + \left( \frac{9}{16} \right) [1 - g(0)] - \left( \frac{16}{5} \right) A \] ... (2.52)

\[ \gamma_0 = 0.25 - \left( \frac{\pi}{24} \right) \left( \frac{4}{9} \pi \right)^{1/3} r_s^2 \frac{d}{dr_s} \left[ r_s^{-2} \frac{d}{dr_s} E_c(r_s) \right] \] ... (2.53)

Here \( g(0) = \frac{Z'}{8 I_1(Z')} \) ... (2.54)

where \( I_1(Z') \) is the modified Bessel function of first order and \( E_c(r_s) \) is the correlation energy.

A notable feature of this function is its involvement of the logarithmic singularity at \( q \approx 1.94 k_F \). Some of the other functions due to Hubbard [49], Geldart and Vosko [52], Singwi - Sjölander - Tosi - Land [56] and Vashistha - Singwi [61] do not exhibit such a feature. Figures 2.1 and 2.2 show the local field functions \( f(q) \) of Ichimaru and Utsumi and Taylor plotted against \( q / k_F \) for five alkali metals viz. Li, Na, K, Rb and Cs and polyvalent metals Al and Pb.

The selection of the Hartree local field function along with those of Taylor and Ichimaru and Utsumi allows us to study the relative influence of the exchange and correlation effects in various properties exhibited by solids and liquids. This is because the different forms of local field functions give varying contribution to the form factors.
Figure 2.1: Ichimaru–Utsumi screening function.
Figure 2.2: Taylor's screening function.
It has been observed that a unique method of determination of the parameter of the potential has not been used by many investigators. The parameter is generally found by fitting to some experimental result. 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. Also the parameter could be determined from the \( q = q_0 \) value [39,45]. These methods of finding the potential parameter does not, however, satisfy the fundamental condition

\[
\frac{dE}{d\Omega_0} = - P = 0 \quad \ldots (2.55)
\]

This condition states that the total energy of a metal must have a minimum for that volume of the primitive cell which is observed experimentally. It's violation leads to the lattice, in fact, being studied under pressure, which can noticeably affect it's properties, particularly the compressibility and longitudinal vibration branches.

In the present study we have found the potential parameter by satisfying the equilibrium condition given by equation (2.55). The further details regarding the use of condition are discussed in Chapter 3 where the total energy and pressure are computed for simple metals. Once the parameters of the potential are found the calculations of the form factors becomes quite straight forward. The potential parameters found by satisfying the zero pressure condition which are used in the calculations are tabulated in Table 2.2, along with other constants used in the computations.
Table 2.2: Potential parameters found from zero pressure condition and other constants and parameters used in the computations.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Structure</th>
<th>$Z$</th>
<th>$\Omega_0$ (a.u.)</th>
<th>$k_F$ (a.u.)</th>
<th>$r_s$ (a.u.)</th>
<th>$r_c$ (a.u.)</th>
<th>H</th>
<th>T</th>
<th>IU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>BCC</td>
<td>1</td>
<td>144.9</td>
<td>0.5890</td>
<td>3.258</td>
<td>0.8142</td>
<td>0.8078</td>
<td>0.8104</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>BCC</td>
<td>1</td>
<td>254.5</td>
<td>0.4882</td>
<td>3.931</td>
<td>1.0786</td>
<td>1.0729</td>
<td>1.0752</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>BCC</td>
<td>1</td>
<td>481.4</td>
<td>0.3947</td>
<td>4.862</td>
<td>1.4433</td>
<td>1.4408</td>
<td>1.4417</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>BCC</td>
<td>1</td>
<td>587.9</td>
<td>0.3693</td>
<td>5.197</td>
<td>1.5752</td>
<td>1.5747</td>
<td>1.5747</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>BCC</td>
<td>1</td>
<td>745.5</td>
<td>0.3412</td>
<td>5.625</td>
<td>1.7447</td>
<td>1.7474</td>
<td>1.7460</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>FCC</td>
<td>3</td>
<td>111.3</td>
<td>0.9276</td>
<td>2.069</td>
<td>0.61745</td>
<td>0.56659</td>
<td>0.55607</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>FCC</td>
<td>4</td>
<td>203.4</td>
<td>0.8350</td>
<td>2.298</td>
<td>0.83575</td>
<td>0.75768</td>
<td>0.73512</td>
<td></td>
</tr>
</tbody>
</table>

It is evident from this Table 2.2 that the parameter obtained by IU function falls within those obtained by H and T. In addition, it is also noticed that the parameter is not much sensitive to the screening function in the cases of monovalent alkali metals while it is highly influenced by the exchange and correlation effects in the cases of polyvalent metals. The variation of the potential parameter $r_c$, found by satisfying the zero pressure condition for all the seven simple metals pursued in the present study, against ($\Omega_0 / Z$) is plotted in Figure 2.3 for IU screening function. The variation is similar in case of the other two screening functions as well.
Figure 2.3: Variation of $r_e$ against $\Omega_o/Z$
It is observed that the relation between \( r_c \) and \( (\Omega_0 / Z) \) can be given by a second degree polynomial. The fitting equations for the three screening functions obtained are given below.

\[
\begin{align*}
    r_c (H) &= 0.6165 + 0.0019416 (\Omega_0 / Z) - 5.53463 \times 10^{-7} (\Omega_0 / Z)^2 \quad \ldots (2.56) \\
    r_c (T) &= 0.5495 + 0.0022312 (\Omega_0 / Z) - 8.30701 \times 10^{-7} (\Omega_0 / Z)^2 \quad \ldots (2.57) \\
    r_c (IU) &= 0.5324 + 0.0023261 (\Omega_0 / Z) - 9.34387 \times 10^{-7} (\Omega_0 / Z)^2 \quad \ldots (2.58)
\end{align*}
\]

Such a relation may be of great help while studying systems with slightly different atomic volumes (while incorporating changes in crystal temperatures) or while handling binary alloys having a different atomic volume than both the constituent metals which make up the alloy. Instead of satisfying the zero pressure condition every time one can simply use the potential parameter obtained from such a relation.

After evaluating the parameters of the potential the model potential is plotted in real space as shown in Figure 2.4. It can be inferred from Figure 2.4 that as the atomic volume increases the size of the core increases while the depth of the potential decreases. So it is also interesting to find out the relation between the depth of the potential and the atomic volume.
Figure 2.4: $W(r)$ against $r$ for some simple metals.
Finally the form factors are plotted in Figures 2.5 and 2.6. A study of the form factors give a correct limiting values of $- (2/3) E_F$ (required for a local pseudopotential [15]) as $q \to 0$, i.e.

$$
\lim_{q \to 0} W(q) = \frac{2}{3} E_F \quad \ldots (2.59)
$$

where $E_F$ is Fermi energy.

All the form factors are free from unnecessary oscillations at large $q$ values. It can also be observed that the effect of exchange and correlation is dominant at small $q$ values while beyond $q_0$ the form factors have almost equal values which will give accuracy in the region of more interest for physical properties.

The form factors presently computed are employed in the comprehensive study of various physical properties of simple metal in the solid and liquid phases, binary alloys and metallic glasses in the following chapters of the thesis.
Figure 2.5: Form factors for Alkali metals.
Figure 2.6: Form factors for Al and Pb.