CHAPTER II

PSEUDOPOTENTIAL THEORY AND DIELECTRIC SCREENING

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2.1 Introduction

The first requirement in describing a dense fluid of interacting electrons and ions is, of course, a knowledge of the interactions. We consider here the nature of the electron-ion interaction, the quantity which most clearly distinguishes simple metals from other metals. We suppose that the electrons can be unambiguously classified as "valence" or "core" electrons, the latter being so tightly bound that their degrees of freedom can be largely ignored [1] in calculating the thermodynamics of the liquid. The (unscreened) single-particle interaction between an ion and an electron in a simple metal (liquid) is characterized by a potential $V(r)$ of the form shown schematically in figure 2.1. $V(r) \sim -\frac{Ze^2}{r}$ outside the core, while within it $V(r)$ is strongly negative and nonconstant. Because of its strength $V(r)$ is not amenable to treatment by perturbation theory, and it is thus paradoxical that the valence electrons in simple metals should behave for so many purposes like free particles. The paradox is resolved within the framework of pseudopotential theory, and summarize those aspects of the argument which are relevant for present purposes.

The notion of the pseudopotential was first introduced in the solid state physics by Phillips and Kleinman [2] and by Antoncik [3] in the study of energy band structure of semi-conductor. The electron wave functions do not at all
Figure 2.1 Schematic representation of an electron ion potential in a simple metal.
resemble plane waves near cores so the effect of the potential upon the wave functions is very large. At the same time, the effect of the potential on the energy bands turns out to be small. This paradox is very nicely resolved by the idea of a pseudopotential that represents the effect of the potential upon the bands themselves. The smallness of these pseudopotentials allows us for many purposes to treat it as a perturbation and to calculate many more properties of a simple metal than is possible for any other state of condensed matter. Herring [4] proposed the orthogonalized plane wave (OPW) method which is an improvement on the plane wave method of energy band calculations in a solid. He observed that the conduction electron states contain many oscillations in the region of the core and pointed out that the conduction electron states are orthogonal to each of the core states. The interaction of the electrons with the metallic ions had only a small effect on the electron energies. The central idea of the pseudopotential theory is to replace the deep ion core potential by a shallow pseudopotential which is chosen such that energy eigen values of the pseudowave equation for metal is same as that of the exact wave equation. The pseudowave function has no radial nodes but has a rapidly convergent series of plane-waves to give the real energy band structure. In other words, a correct pseudopotential is defined as one that gives the same energy levels as the real potential, at least for a range
of states of interest. Detailed discussion of the pseudopotential formalism and its application are available in review article of Harrison [5], Cohen and Heine [1] and Ziman [6]. A brief discussion of the pseudopotential formalism is given in the section 2.2.

2.2 Pseudopotential Formalism

On the basis of OPW method Phillips and Kleinman [2] and Antoncik [3] observed that the requirement of orthogonalization of valence electron wave functions to the core state wave functions, might be replaced by introducing a repulsive potential. The pseudopotential formulation is based on the two assumptions both of which are used in the energy band calculations:

(i) The many electron problem is replaced by a self-consistent-field problem in which the effects of the interactions between electrons are included as a self-consistently determined potential field which includes a self-consistent field for exchange.

(ii) The electronic states are divided into core and conduction-band states and will assume that the core states are the same as in free atoms. At a later stage additional approximations are made, based upon the fact that the calculated pseudopotential is small. In the simple metals the weakness of the pseudopotential will be used in the self-consistent determination
of the potential itself. Further, a system consisting of the core and one extra valence electron is considered. If $V$ is the self-consistent potential seen by a valence electron including the electron-electron interaction, the Schrödinger equation is given by

$$H\Psi_V = [T + V]\Psi_V = E_V\Psi_V \quad (2.1)$$

where $T$ is the electron kinetic energy operator and $E_V$ is the energy eigenvalue for the state, $\Psi_V$ is the wave function. Now when an electron comes in the vicinity of an ion, it experiences an additional potential $V_R$ other than $V$, which is repulsive in nature. The repulsive potential arises due to the effect of conduction electrons on the core electrons. Thus the resultant effect of these two potentials, which are opposite in nature, is very small. This net effective potential is termed as pseudopotential. The quantum mechanical pseudopotential equation may be written (using equation (2.1)) as

$$(H + V_R)\varphi_V = (T + V + V_R)\varphi_V = E_V\varphi_V \quad (2.2)$$

where $(H + V_R)$ is known as the pseudo-Hamiltonian and $(V + V_R)$ is the pseudopotential and $\varphi_V$ is the pseudo wavefunction. The true conduction electron wavefunction $\Psi_V$ is related with pseudowave function as

$$\Psi_V = \varphi_V - \sum_\alpha b_\alpha \Psi_\alpha \quad (2.3)$$
where $b_\alpha$ are arbitrary coefficients, which are determined by the condition that the conduction electron states are orthogonal to the core states. $\psi_\alpha$ are the core wave functions which can be considered as equal to the atomic orbitals. The summation over $\alpha$ is on all the core states of the atom. Thus in the pseudopotential approach, $V_R$ cancels most of the large negative potential energy $V$ in the core region and generates a weak potential $W = (V + V_R)$ in the resulting Hamiltonian. Another advantage of the pseudopotential is that the pseudowave function $\phi$ is smooth and does not contain rapid oscillations as the actual wave function has in the core region. Hence the pseudopotential equation can be considered as a perturbation of the free electron system and the perturbation theory can be used to calculate the energy eigenvalues of electrons. Equation (2.2) retains the same energy eigenvalues but alters the eigen functions such that the pseudo wave function $\phi$ is identically equal to the real wave function $\psi$ outside the atomic core or some chosen larger radius and then extends smoothly inside the core without the wriggles that $\psi$ possess.

2.3.1 Pseudopotential Form Factor

The pseudopotential form factor plays an important role in the evaluation of the properties of metals. It describes the electron-ion interaction. Various methods
including direct calculations [7] and model or pseudopotential formalism [6] have been developed for the evaluation of effective electron-ion potential in metals. It has also been calculated from the first principle [8] using Hartree-Fock function of the ions or obtained from experimental measurements. Particularly central to this development has been the important contributions of Harrison and Heine groups. Actually there is no accurate method of getting the form factors by which almost all the properties related with electrons and ions may be described for metals. It is generally seen that a particular pseudopotential may be appropriate in some properties for some metals and unsuitable for the other properties. The efforts have been already made about the extension of the pseudopotential theory to cover the wide range of metals. A number of formulations have been presented for determining the pseudopotential or their form factors. Generally a model potential approach is adopted.

2.3.2 Evaluation of the Form Factor

The self-consistent field approximation serves as a basis for the development of a pseudopotential. In this approximation the effect of the interaction of a given electron with all other is replaced by a potential. The Fourier transform of self-consistent potential $V(q)$ is obtained by screening the Fourier transform of the bare ions.
potential $W_b(q)$ through a dielectric screening function $\varepsilon(q)$

$$V(q) = \frac{W_b(q)}{\varepsilon(q)}$$

The determination of screened form factor $V(q)$ involves a knowledge of the bare potential and dielectric screening function. The bare ion pseudopotential can be separated into individual ionic potential centred at the ion position $r_j$ by the relation

$$W_b(q) = \sum_j U(r - r_j)$$

where $U(r)$ is the Hartree-Fock potential of each ion and $r_j$ is the position vector of the $j^{th}$ ion relative to the reference ion. $W_b(q)$ has maximum contribution from $r_j = 0$ and the contributions decrease as we go to farther ions. In terms of its Fourier transform the bare ion potential can be written as

$$W_b(q) = \int W_b(r) e^{iq\cdot r} d^3r = \frac{1}{N} \sum_j e^{iq\cdot r_j} U(q) = S(q) U(q)$$

where $S(q)$ is the geometrical structure factor, which depends upon the lattice structure. In the perturbation expansion, the pseudopotential enters through its plane
wave matrix element $< k + q | \mathbf{W}_b | k >$ which becomes

$$< k + q | \mathbf{W}_b | k > = \mathcal{S}(q) \ U_k(q) \hspace{1cm} (2.7)$$

$U_k(q)$ is the matrix element of the pseudopotential at a single ion site and is given by

$$U_k(q) = N < k + q | \mathbf{U} | k >$$

$$= \frac{1}{a} \int_0^\infty e^{-i(q+k) \cdot r} \ U(r) \ e^{i \mathbf{k} \cdot \mathbf{r}} \ d^3r$$

$$\hspace{1cm} (2.8)$$

where $q = V/N$, the volume per ion. The quantity $U_k(q)$ is known as the form factor. If we restrict ourself to a local model potential, the form factor depends only on $q$ and is independent of $k$. The equation (2.8) then leads to

$$U(q) = \frac{1}{a} \int_0^\infty e^{-i \mathbf{q} \cdot \mathbf{r}} \ U(r) \ d^3r.$$  \hspace{1cm} (2.9)

Considering the limit when $q$ tends to zero, the Fourier transform (2.9) of an ionic potential is always dominated by the Coulombic part outside the pseudizing radius $r_c$

$$U(q \to 0) = - \frac{4\pi Z e^2}{\mathbf{q}^2}.$$ \hspace{1cm} (2.10)

Once potential of the bare ions has been obtained, the bare ions can be planted into an electron gas which then screens them to give total pseudopotential.
2.3.3 Fitting Procedure of the Form Factor

For metals the shape of Fermi surface is the best source of information, since it can be measured with considerable precision. Various technique of measurements of Fermi surface have been described by Sheonberg [9]. The most precise data about the Fermi surface are furnished by de Haas-Van Alphen effects, which measures the maximum or minimum area of cross-section if the Fermi surface is sanctioned by planes perpendicular to the magnetic field. The pressure dependence of de Haas-Van Alphen effect furnishes the additional data $dA/dV$ (change in area with respect to volume), which can also be fitted by the pseudopotential method. Details of the fitting procedure of a pseudopotential to the Fermi surface data are presented by Ashcroft [10], Kimball et al [11], Ashcroft and Lawrence [12], Khanna and Khandelwal [13] and Khanna [14].

Another device which is also widely employed in the fitting of pseudopotential form factor $U(q)$ to an observed phonon spectrum [15]. A phonon spectrum contains a lot of information about $U(q)$, extending over the whole range of momentum transfer $q$ instead of being limited to a few points at the reciprocal lattice vector $G$. Another feature of phonon spectrum is that it measures the logarithmic singularity in the dielectric function at $q = 2k_F$, which results in Kohn Kinks [16]. Generally the form factor is fitted to the observed frequency of phonon spectra at the (100) point.
of the longitudinal branch.

Among the other fitting methods are the optical absorption spectrum [17], soft X-ray spectra [18] and liquid metal resistivity [19]. Among these the resistivity of liquid metal has been the most favourite quantity for the pseudopotential fittings. The reason is that it is easy to calculate at least for simple metals and the theory is reasonably well understood [19, 20]. It should be necessary to point out that liquid metal resistivity is quite sensitive to $U(q)$ in the region less than but near $2k_F$.

2.4 Dielectric Screening

The dielectric formulation of many-body problem has been found very fruitful in studying the metallic properties which depends strongly on electron-electron interactions. It results in elimination of the long range Coulomb field of the ion. In setting up the potential seen by a conduction electron in the metal, one has to allow for the effects due to interaction between different electrons and of self-consistent screening of bare ion pseudopotential. Bardeen [7] first introduced a self-consistent method for treating the screening by the electrons in the Hartree approximation in connection with the study of the electron-photon interaction. Lindhard [21] has also derived a similar expression using the random-phase approximation (RPA). The dielectric
function can be written as

\[ \varepsilon(q) = 1 + \frac{4\pi Z e^2}{aq} \left( \frac{2}{3} E_F \right) X(q) \]  

(2.11)

where

\[ X(q) = \frac{1}{2} + \frac{4k_F^2 - q^2}{8q k_F} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \]  

(2.12)

\( Z \) is the valence of the metal, \( e \) the electronic charge, \( E_F \) the Fermi energy, \( k_F \) the Fermi momentum. The equation (2.11) referred to as the Hartree-dielectric function, includes the interaction between electrons, but ignores the exchange and correlation effect. It's validity is limited to the high electron density region. There have been many efforts towards obtaining the dielectric function in an approximation beyond RPA. Hubbard [22] introduced the contribution of exchange and correlation in the Hartree dielectric function and deduced

\[ \varepsilon^*(q) = 1 + \left[ \varepsilon_H(q) - 1 \right] \left[ 1 - f(q) \right] \]  

(2.13)

where \( \varepsilon_H(q) \) is the same as equation (2.11) and \( f(q) \) is the expression taking into account of exchange and correlation energy. Thus the calculation of \( \varepsilon_H(q) \) is straightforward [23] in the one electron theory, but there is some uncertainty about the best approximation for \( f(q) \). Various workers have adopted different procedures to calculate the exchange and correlation energy and have obtained different expressions
for \( f(q) \). We shall describe here only the results obtained by some workers.

2.4.1 Exchange and Correlation Functions; Geldart-Vosko

The screening function of an interacting electron gas at high and metallic densities is investigated by many-body perturbation theory. The analysis is guided by a fundamental relation between compressibility of the system and the zero-frequency small wave vector screening function (i.e., screening constant). In the theoretical description of a variety of properties of metals, the polarizability of the conduction electrons plays a central role. The dielectric properties of a non-interacting electron gas, which is appropriate for high densities, have been studied extensively. However, at metallic densities, the effect of electron-electron interaction on the polarizability is expected to be large.

The dielectric function in quantum mechanical case is given by

\[
\varepsilon(q, \omega) = 1 - \frac{V(q) X(q, \omega)}{1 + V(q) f(q) X(q, \omega)} \tag{2.14}
\]

here

\[
V(q) = \frac{4\pi e^2}{q^2} \tag{2.15}
\]

and \( X(q, \omega) \) being the usual free-electron polarizability (usual Lindhard function).
Geldart and Vosko [24] gave an expression for exchange and correlation energy which satisfies the compressibility sum rule, and provides a negative value of the pair correlation function. The expression for \( f(q) \) is given by

\[
f(q) = \frac{q}{2(q^2 + \xi k_F^2)}
\]

with

\[
\xi = \frac{2}{(1 + 0.026 r_s)}
\]

and hence

\[
f(q) = \left( 0.25 + \frac{0.153}{4\pi k_F^3} \right)
\]

2.4.2 Exchange and Correlation Function : Vashishta-Singwi

Vashishta and Singwi [25] presented a modification of the theory of Singwi et al [26,27], which has the merit of satisfying almost exactly the compressibility sum rule and of giving a pair correlation function \( g(r) \) of the same quantity as in Singwi et al [26]. This modification consists in allowing for the change in the pair correlation function in an external weak field via the density derivative of the equilibrium pair correlation function \( g^0(r) \). This then result in an additional term involving the density derivative of \( g^0(r) \) in the local field correction of Singwi et al [26]. Since the density derivative of \( g^0(r) \) is related
to the three particle equilibrium correlation function, it is in this sense that three particle correlations are built into new local field expression. It is this later feature which is believed to be very important and which will have significant consequences, on the calculated annihilation rate of positrons in heavier alkali metals in which Coulomb corrections are very important. The new term in the local field correction, as anticipated, gives an important contribution to the \( q \rightarrow 0 \) behaviour of the static dielectric function \( \varepsilon(q, 0) \) and at the same time has an almost insignificant effect on the very large-\( q \) behaviour of \( \varepsilon(q, \omega) \). In all calculations of lattice dynamics, it is imperative that the dielectric response function satisfies the compressibility sum rule. The calculations with frequencies much lower than the plasma frequency, the present static approximation is very good. Since the dielectric function occurs in the calculation of a variety of metallic properties, a self-consistent values of \( f(q) \) for \( q \leq 2k_F \) can be fitted quite well with a simple function of the form

\[
f(q) = A \left[ 1 - e^{-B(q/k_F)^2} \right]
\]

(2.19)

where \( A \) and \( B \) are the parameters depending upon the inter-electron distance.
Table 2.1: Parameters A and B for Alkali Metals for Different Values of $r_s$

<table>
<thead>
<tr>
<th>Metal</th>
<th>$r_s$</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>4.04860</td>
<td>1.0894390</td>
<td>0.28353</td>
</tr>
<tr>
<td>K</td>
<td>5.02628</td>
<td>1.1823679</td>
<td>0.26808</td>
</tr>
<tr>
<td>Rb</td>
<td>5.37239</td>
<td>1.2152657</td>
<td>0.26261</td>
</tr>
<tr>
<td>Cs</td>
<td>5.78495</td>
<td>1.2544795</td>
<td>0.25609</td>
</tr>
</tbody>
</table>
2.4.3 Exchange and Correlation Function: Ichimaru-Utsumi

The frequency and wave number dependent, longitudinal dielectric function [28], $\varepsilon(q, \omega)$ is an essential quantity for the description of the electronic properties of metals and related substances such as the laser-compressed plasmas and the interior of heavy planets. The electrons (with number density $\rho$) in such a system usually form a strongly coupled system in that the Coulomb coupling constant $r_s = (3/4\pi\rho)^{1/3}$ $\text{me}^2/h^2$ is greater than unity. A simple fitting formula for the dielectric function of strongly coupled degenerate electron liquids is used which satisfies a number of self-consistency conditions and which accurately reproduces the recent Monte-Carlo results [29] as well as those of the latest microscopic calculations [30]. The result should be of use to numerical studies of the strong coupling effects involving degenerate electron liquids. The local field exchange and correlation function $f(q)$ proposed by Ichimaru and Utsumi (IU) [31] is

$$f(q) = 0.25 + \frac{\nu_1 \nu_2}{\nu_3} \quad (2.20)$$

where $\nu_1$, $\nu_2$ and $\nu_3$ are defined in IU [31].
Table 2.2: Calculated Values of $\nu_1$, $\nu_2$ and $\nu_3$ for Alkali Metals at their Melting Temperature

<table>
<thead>
<tr>
<th>Metal</th>
<th>T(K)</th>
<th>$\nu_1$</th>
<th>$\nu_2$</th>
<th>$\nu_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>371</td>
<td>5255.0463</td>
<td>0.4121</td>
<td>69940.9799</td>
</tr>
<tr>
<td>K</td>
<td>337</td>
<td>7008.0611</td>
<td>0.5116</td>
<td>99309.1286</td>
</tr>
<tr>
<td>Rb</td>
<td>312</td>
<td>7670.2537</td>
<td>0.5468</td>
<td>110956.6093</td>
</tr>
<tr>
<td>Cs</td>
<td>301</td>
<td>8487.4395</td>
<td>0.5888</td>
<td>125715.8460</td>
</tr>
</tbody>
</table>
2.5.1 Ashcroft Model Potential

The problem of establishing the effective electron-ion interaction in a metal either from first principle or as a pseudopotential has been one of the considerable and continuing interest. Detailed knowledge of this quantity is essential for the determination of the fundamental properties of metals including for example band structures, Fermi surfaces, transport and equilibrium properties. Model forms for the interaction expressed as a pseudopotential has been proposed by Cohen [32] and Heine and Abarenkov [33]. In its unscreened form the latter comprises a basic Coulomb potential outside a chosen radius $R_M$ and is represented by a sequence of square wells indexed according to the angular momentum $l$ inside this radius. The strengths of the wells are determined from spectroscopic data taken from the free atom and are subsequently extrapolated to the energy of solid.

The pseudopotential transformation (i.e. from $\psi$ to $\psi_{ps}$) leads to terms which cancel the strong Coulomb like potential in the core region while leaving the potential essentially unaltered outside. It is considered that effective radius at which the change in the nature of pseudopotential develops little if any change in the core states occurs in the simple metals. It is expected that pseudopotential cancellation to occur principally within a volume defined by the extent of core states. On the scale of usual atomic volume this quantity
is small in the simple metals, perhaps only a few percent. Relative to the Coulomb term this is just the factor that weights the core terms in the Fourier transform of the effective potential. Further, if $R_{\text{core}}$ is the neighbourhood of the ion-core radius, then since the effective potential is weak in $r < R_{\text{core}}$ [34]. With these considerations in the mind it is appealing to use a limited effective $r$-space potential of the Ashcroft form [35],

$$V_{\text{eff}}(r) = -\frac{Ze^2}{r} \quad r > R_{\text{core}}$$  \hspace{1cm} (2.21)

$$V_{\text{eff}}(r) = 0 \quad r < R_{\text{core}}$$

where $R_{\text{core}}$ is expected to be close to the usual ionic radius. Assuming that the real potential $V$ is basically Coulombic outside $R_{\text{core}}$. Equation (2.21) may be regarded as a local approximation of the Austin form [36]. Further assuming that the result of the core space projection manifests itself as an effectively complete cancellation of the real potential in $r < R_{\text{core}}$. $R_{\text{core}}$ is indeed close to $R_{\text{ionic}}$ [37].

The linear screening of equation (2.21) is postulated by the gas of conduction electrons and take the static dielectric function to be of the form

$$\varepsilon(x) = 1 + \frac{\lambda^2 f(x)}{x^2} \quad (2.22)$$
where \( x = k/2k_F \) and \( \lambda^2 = (\pi a_0 k_F)^{-1} \). The function \( f(x) \) may be written

\[
f(x) = F(x) \cdot g(x)
\]

where \( F(x) \) is the Lindhard function, and \( g(x) \) is the correction for exchange. The form factor of equation (2.21) becomes

\[
U(x) = \frac{(-\cos Sx) \lambda^2}{x^2 + \lambda^2 f(x)}
\]

in units of \( 2/3 k_F \) which for linear screening is the known longwavelength limit for scattering on the Fermi surface.

In equation (2.24), \( S = 2k_F R_{\text{core}} \) is the quantity which determines the location of the first node of pseudopotential.

2.5.2 Heine and Abarenkov Model Potential

Heine and Abarenkov [33,38] proposed a method of setting up the model potential from the point of view of the quantum defect method. In this method the ion potential is replaced by an energy and wave number dependent square well. It is noted that the calculation of the eigen state or eigenvalue for an atom, whether it be a free atom or an ion in the lattice, may be divided into two regions: the core region and the region outside the core. A sphere is constructed surrounding the core separating the two regions. Then a calculation of the wave function might be carried out by calculating the wave function within this model sphere and outside the model sphere (Heine and Abarenkov model [33]) and
matching them smoothly. Therefore the only information used to construct the wave function outside the sphere is the value and slope of the wave function at the cell surface as determined by an integration within the sphere. The wave functions are expanded in both regions in spherical harmonics and only the logarithmic derivative of each component of the wave function at the sphere influences the wave function outside the sphere. Thus the same wave function, and therefore the same energy, would be obtained (except for normalization) outside the sphere if the true ion potential were replaced inside the sphere by a flat potential leading the same logarithmic derivative. This flat potential would necessarily depend upon the angular momentum quantum number $l$ and the energy $E$. This potential is chosen such that there are no nodes in the wave function within the sphere. The procedure then is to replace strong core potentials by these model potentials within the sphere at every ion. A sphere of a chosen radius $R_M$ is considered around the ion, outside which the potential is Coulombic. The model potential is described by the relation

$$V_M(r) = \sum_l A_l(E) P_l, \quad \text{for } r < R_M$$

$$= -\frac{Ze^2}{r}, \quad \text{for } r \geq R_M$$

(2.25)

where $A_l$ is (independent of $r$) an energy parameter, which varies slowly with energy $E$ of the conduction electrons as well as the model radius $R_M$ and $P_l$ is the projection operator
which picks out the partial wave from the incident wave. Thus \( V_M \) is simply an \( l \)- and \( E \)-dependent operator. The form factor of the model potential is given by

\[
\langle k + q | V_M | k \rangle = \frac{4\pi}{\Omega} (2l+1) A_1(E) P_l(\cos \Theta) \int_0^{R_M} j_1(k'r)j_1(kr)r^2 dr
\]

\[-(4\pi Ze^2/\Omega q^2) \cos (q R_M) \]

(2.26)

where \( \Theta \) is the angle between \( k \) and \( k' \) (\( k' = k+q \)).

The model potential was widely applied in the evaluation of several metallic properties \([39,40]\). The potential in real sense is non-local in nature. Animalu and Heine \([41]\) extended the Heine and Abarenkov (HA) model potential by introducing exchange and correlation correction between the electron orthogonality correction and non-local screening of electrons. They divided the effective potential into the local part and non-local part plus the orthogonality and correlation corrections.

### 2.5.3 Shaw Model Potential

The model potential proposed by Heine and Abarenkov was modified by Shaw \([42,43]\) under following considerations:

(i) The ion core potential was replaced with an \( A_1(E) \) for all values of \( l \) from zero to infinity.

(ii) The model radius \( R_1(E) \) was considered to depend on \( l \) and on \( E \).
Thus Shaw proposed a non-local and energy dependent model potential. The non-locality of the model potential is important, particularly for quantitative purposes in the evaluation of the structure dependent energies or interionic interactions [44,45].

The bare ion model potential of Shaw consists of a local Coulomb interaction and a non-local part

\[ W_0(r,E) = -\frac{2\pi}{r} - \sum_{l=0}^{l_0} \Phi[R_1(E)-r](A_1(E) - \frac{2\pi}{r})|l>|l| <1| \]  

(2.27)

where \( \Phi(r) \) is the step function defined by

\[ \Phi(r) = \begin{cases} 1 & r \geq 0 \\ 0 & r < 0 \end{cases} \]  

(2.28)

and the \( |l> \) are a set of angular momentum eigenstates of the core electrons and \( l_0 \) is its highest quantum number.

The model well depth \( A_1(E) \) and its radius \( R_1(E) \) are related by

\[ A_1(E) = \frac{2\pi}{R_1(E)} \]  

(2.29)

The form factor for this model potential is given by

\[ W_0(k,q) = e^{-1} \langle k+q | W_0 | k \rangle = V_c(q) + f(k,q) \]  

(2.30)

where

\[ V_c(q) = -\frac{8\pi Z}{\Omega_0 q^2} \]
and
\[ f(k, q) = -\frac{8\pi^2}{\Omega_0} \sum_{l=0}^{1} (2l+1) P_l(Cos\theta) R_1^2 \int_0^1 dx x(x-1) j_1(kR_1x)j_1(k'R_1x) \]

where \( k' = k+q \).

The screened form factor can be written as the sum of the Hartree term and the correction term due to many electron exchange and correlation effects [42]

\[ W(k, q) = W_H(k, q) + \Delta W(q) \tag{2.31} \]

where
\[ W_H(k, q) = \frac{V_c(q) + V_d(q)}{\varepsilon_H(q)} + f(k, q) + g(q) \tag{2.32} \]

and
\[ \Delta W(q) = -\frac{f(q)}{\varepsilon(q)} [W_H(k, q) - W_0(k, q)] \tag{2.33} \]

In equation (2.32) \( V_d(q) \) is a local contribution due to the depletion hole charge \( \rho_d \),
\[ V_d(q) = \frac{8\pi^2}{\Omega_0} \frac{\rho_d}{q^2} \tag{2.34} \]

\( \varepsilon_H(q) \) is the Hartree screening function and \( g(q) \) represents the non-local screening contribution,
\[ g(q) = \frac{4}{\pi^2 q^2 \varepsilon_H(q)} \int_{k<k_F} dk' \frac{f(k, q)}{k^2 -(k+q)^2} \tag{2.35} \]
In equation (2.33) \( f(q) \) is a function which describes exchange and correlation effects approximately and the electron screening function is given in terms of \( f(q) \) by equation (2.13). In deriving an expression for the effective ion-ion interaction \( \phi(x) \), some care must be taken of the energy dependence of a model potential and thus of the treatment of \( \rho_d \). It is convenient to include \( \rho_d \) in the valence \( Z \) and treat each ion as carrying an effective charge \( Z^* = Z - \rho_d \) \footnote{43}. Within second order theory, \( \phi(x) \) is given by the sum of a direct Coulomb interaction between ions with valence \( Z^* \) and an indirect one through the conduction electrons. Thus

\[
\phi(x) = \frac{2(Z^*)^2}{x} \left(1 - \frac{2}{\pi} \int_0^\infty dq \, F_N(q) \frac{\sin qx}{q}\right) \quad (2.36)
\]

where \( F_N(q) \) is the normalized energy-wavenumber characteristic and can be written similarly to equation (2.31)

\[
F_N(q) = F_N^H(q) + \Delta F_N(q) \quad (2.37)
\]

The Hartree term is given by

\[
F_N^H(q) = \left( \frac{q^2}{8 \pi Z^*} \right)^2 \left[ - \frac{4}{\pi^2} \int_0^q dq \, k \sqrt{k^2 - (k+q)^2} \right]
\]

\[
+ \left( \frac{4}{\pi^2} \int_{k_F}^q dq \, \frac{W_H(k, q)}{k^2 - (k+q)^2} \right)^2 \quad (2.38)
\]
and the correction term by

$$\Delta F_N(q) = \left( \frac{q^2}{8\pi Z^2} \right)^2 \frac{\varepsilon(q)}{\varepsilon(q)} f(q) \left[ W_R(k,q) - W_0(k,q) \right]^2$$  \hspace{1cm} (2.39)

2.6.1 Energy-wavenumber Characteristic

In pseudopotential theory the energy-wave number characteristic $F(q)$ is of prime importance and many metallic properties such as binding energy and ion-ion interaction etc. require the knowledge of this function $F(q)$. Several attempts have been made to calculate this quantity for simple metals. Harrison [46] applied the model potential form factors determined from measured phonon dispersion relation to compute the energy-wavenumber characteristic

$$F(q) = - \frac{q^2}{8\pi e^2} \frac{[\varepsilon(q) - 1]}{\varepsilon(q)} \frac{|W_b(q)|^2}{1 - f(q)}$$  \hspace{1cm} (2.40)

where $\varepsilon(q)$ is the Hartree dielectric function, $W_b(q)$ the bare-ion pseudopotential form factor. This quantity can also be expressed in terms of the electronic band structure energy function $G(q)$, Cochran [47]. This function, which is very important in the description of several properties like ion-ion interaction, is defined as

$$G(q) = - \frac{q^2}{2\pi Z^2 e^2} F(q)$$  \hspace{1cm} (2.41)
In view of equation (2.40), we get

\[
G(q) = \left[ \frac{4\pi Z e^2}{\Omega q^2} \right]^{-2} \frac{\left[ \varepsilon(q) - 1 \right]}{\varepsilon(q)} \left\{ \frac{\frac{1}{\varepsilon(q)} - \frac{1}{\varepsilon(q)} - \frac{1}{\varepsilon(q)}}{1 - f(q)} \right\}^2 (2.42)
\]

The energy-wavenumber characteristic depends on the model potential applied and the dielectric function. The latter, in turn, depends upon the exchange and correlation function \( f(q) \) through \( F(q) \). The Hartree dielectric function modified and used as

\[
\varepsilon(q) = 1 + \frac{4\pi Z e^2}{\Omega q^2} [1-f(q)] - \frac{3}{2F} \left[ 0.5 + \frac{(4 k_F^2 - q^2)}{8q k_F} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right] (2.43)
\]

The various workers have adopted different procedures to calculate the exchange and correlation energy and have obtained different expressions for \( f(q) \) \([24,25,31]\).

2.6.2 Interionic Potential

The interionic potential between the ions or atoms of metals is of central significance for a detailed study of various microscopic properties of a substance. Conduction electrons play a major role in the interaction between the ions. In the pseudopotential approach, this potential is described as a pairwise central interaction between ions. The pairwise interaction consists of a direct Coulomb term and an indirect ion-electron-ion interaction which depends on
the pseudopotential form factor and dielectric screening. 
Thus the electronic effects on the ion-ion interaction is 
included in terms of a modified pairwise interaction 
between ions. The procedure for calculating the modified 
pairwise interaction is based on writing the total energy 
per ion of the system, including the ion-ion interaction, 
electron-ion interaction and electron-electron interaction 
in Hartree approximation. Thus the total energy consists of 
different contributions:

(i)  The electrostatic interaction between the ions with 
valence charge Ze embedded in a compensating uniform 
background of negative charges.

(ii) The modified free electron energy which depends upon 
the total volume and is independent of the co-ordinates 
of the ions.

(iii) The band structure energy which depends upon the ion 
configuration and the effective potential felt by a 
valence electron.

The expression for total energy can be written as

$$E = \frac{1}{2N} \sum_{i \neq j} \frac{(Ze)^2}{|R_i - R_j|} - \frac{2\pi(Ze)^2}{a} \sum_q \left[ S^*(q) S(q) - \frac{1}{N} \right] \frac{G(q)}{q^2}$$

(2.44)

where G(q) is the electronic band structure energy given as
This is the modified pairwise ion-ion interaction and includes ion-ion, ion-electron and electron-electron interaction. Hence the modified interionic potential can be written as

\[ V(r) = \left( \frac{Z e}{r} \right)^2 - \frac{2(Ze)^2}{n} \int_0^\infty G(q) \frac{\sin qr}{qr} dq \]  

(2.46)

The characteristic feature of the interionic potential is the presence of long-range oscillations which are manifestation of the Friedel oscillations. For large values of \( r \)

\[ V(\text{at large } r) \rightarrow IV(q)^2 \frac{[\cos(2k_F r)]}{q=2k_F \frac{1}{(2k_F r)^3}} \]

(2.47)

Harrison [46] has shown that the effective ion-ion potential can be obtained from the normalized energy-wave number characteristic of a metal in a pseudopotential approach. Shyu and Gaspari [48] used the model potential of Heine and Abarenkov [33] and Ashcroft [35] to calculate the interionic potential of alkali metals. These studies show that the interionic potential is entirely of a screened nature. The many electron effects are also found to drastically change the shape of the interionic potential. Rasolt and Taylor [49] emphasized that the characteristic feature of the interionic potential is the presence of the long-range oscillations which
are the manifestation of the Friedel oscillation in the charge density and even the first well is basically a Friedel oscillation. Thus it is better to achieve the interionic potential through the fitting to charge density. The equations (2.45) and (2.46) show that the interionic potential \( V(r) \) depends upon the model potential \( W_b(q) \) and exchange-correlation function \( f(q) \) through the dielectric constant \( \varepsilon(q) \).
2.7 References


[38] I. Abarenkov and V. Heine, Phil. Mag. 12 (1965) 529.


