PSEUDOPOTENTIAL AND ITS SCREENING

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2.1 PSEUDOPOTENTIAL THEORY:

In this section, attention is given to those aspects of pseudopotential which are vital for their intelligent and effective use. As one might have summarized, for practical purpose it is not necessary to be familiar with the details of the basic derivations and mathematical justification of the general theory of pseudopotentials. Nevertheless, even the practical user of pseudopotentials should not disdain the benefits derived from the basic work on the theoretical understandings of pseudopotential theory. First, it gives vital insight into the construction of simple, but successful, models for the pseudopotential. Second, it provides a feeling of confidence to the practical user of pseudopotentials in absence of what would otherwise seem justified.

The pseudopotential method is a technique for solving the Schrödinger equation and contains essential features of the behavior of electrons in simple metals. To solve the Schrödinger equation for condensed aggregates of atoms, space can be divided into two regions with quite different properties. (i) The regions near the nuclei, called "core regions", are composed primarily of tightly bound core electrons, which respond very little to the presence of neighboring atoms. (ii) While the remaining volume contains the valence electron density which is involved in the bonding together of the atoms. Although the potential in the core is strongly attractive for valence electrons, the requirement that the valence wave functions be orthogonal to those of the core, produces large kinetic energy, which contributes an effective repulsive potential for the valence states [6-14].

The total Hamiltonian, $H_T$, and corresponding Schrödinger equation for a system of $N$ ions and $N'$ electrons, neglecting external interactions, is written as [6],

P. N. Gajjar - Ph.D. Thesis (Physics) - 1996.
\[ H_T = H_i + H_e \]  \hspace{1cm} (2.1)

\[ H_T \psi_T = E_T \psi_T \]  \hspace{1cm} (2.2)

Here subscripts e and i denote electrons and ions, respectively.

The solution of the equation (2.2) is intractable, and we simplify it with the adiabatic approximation or Born - Oppenheimer approximation. The essence of this approximation is that the electrons readjust themselves so rapidly to a change in ion configuration that the ions are regarded as fixed when solving for the electron energies. This assumption uncouples the electron part of the equation from the ion part. Therefore, the total wave function is separable and is written as,

\[ \psi_T = \psi_i \psi_e \]  \hspace{1cm} (2.3)

Thus the adiabatic approximation allows consideration of the electron problem separately from the ion problem and the conduction electron energy becomes an effective potential energy of the ions [34]. Hence the Schrödinger equation for the electron problem is,

\[ H_e \psi_e = E_e \psi_e \]  \hspace{1cm} (2.4)

In the self-consistent field approximation or one-electron approximation, the Hamiltonian for the electron is written as [6],

\[ H_e = T_e + V(x) \]  \hspace{1cm} (2.5)
where $V(r)$ is the potential that an electron moves in, which is calculated in a self-consistent manner and referred as self-consistent field. Using equations (2.4) and (2.5), the Schrödinger equation for a single electron is written as [6],

$$H_e \Psi_e = \left[ T_e + V(r) \right] \Psi_e = E_e \Psi_e \tag{2.6}$$

If we use the index $t$ to denote core electron states and $j$ to denote the state centered at ion position $r_j$ than we have [6],

$$\left[ T_e + V(r) \right] \Psi_{t,j} = E_{t,j} \Psi_{t,j} \tag{2.7}$$

Here the $\Psi_{t,j}$ are the same as for the free atoms according to our first assumption.

With the above equation established within the constraints of the assumption mentioned, we now restructure it in terms of the pseudopotential formulation. As such the pseudopotential formalism grew out of the Orthogonalized Plane Wave (OPW) method [6,7] of band structure calculations, in which the valence wave functions were expanded in a set of plane waves (PW), which are orthogonalized to all of the core wave functions. We, first, expand the electron wave function in terms of a basis of functions that are constructed to be orthogonal to the core states. Following Harrison [6], we use the notation

$$| k \rangle = \Omega^{-1/2} \exp(ik \cdot r) -- a \ normalized \ plane \ wave,$$

$$| t,j \rangle = \Psi_{t}(r-r_j) -- a \ normalized \ core \ function \ centered \ at \ ion \ position \ r_j,$$
and

\[ <t,j | k> = \Omega^{-1/2} \int d^3r \, \psi_t^*(r-r_0) \exp(ik \cdot r) . \]

Then we write the orthogonalized plane waves, as

\[ |\text{OPW}_k> = (1 - P) |k> , \quad (2.8) \]

where \( P \) is the projection operator, which projects any function onto the core states

\[ P = \sum_j |t,j><t,j| . \quad (2.9) \]

We expand the conduction electron wave function in terms of the orthogonalized plane waves to obtain

\[ \psi = (1 - P) \sum_k a_k |k> , \quad (2.10) \]

where \( a_k \) are the expansion coefficients. If we substitute \( \psi \) in the Schrödinger equation, the solution could be attempted using the standard orthogonalized plane wave method.

We are attempting a different approach and will restructure the equation. We introduce the pseudowavefunction,

\[ \phi = \sum_k a_k |k> , \quad (2.11) \]

so that

\[ \psi = (1 - P)\phi . \quad (2.12) \]
We note that $\Phi$ is an expansion of free electron states and that $\Phi = \Psi$ outside the cores because the projection operator is zero there [6]. Substituting in the Schrödinger equation yields,

$$T_e (1 - P) \phi + V(r) (1 - P) \phi = E (1 - P) \phi ,$$  \hspace{1cm} (2.13)

rearrangement of equation (2.13) gives

$$T_e \phi + V(r) \phi - [ T_e + V(r) ] P \phi + E P \phi = E \phi ,$$  \hspace{1cm} (2.14)

so that

$$T_e \phi + W \phi = E \phi ,$$  \hspace{1cm} (2.15)

where we have defined the operator,

$$W = V(r) - [ T_e + V(r) ] P + E P$$  \hspace{1cm} (2.16)

$\equiv$ the pseudopotential operator.

Using

$$[ T_e + V(r) ] P = \Sigma_{t,j} E_{t,j} | t,j > < t,j | ,$$  \hspace{1cm} (2.17)

we have
\[ W = V(r) + \sum_{t,j} \left( E - E_{t,j} \right) \langle t,j \rangle \langle t,j \rangle , \quad (2.18) \]

which is general expression for the pseudopotential.

The first term on the right hand side of equation (2.18) is due to the potential felt by the valence electron in the core region of ions, which is actually strong and attractive. As second term in equation (2.18) represents the repulsive potential, for many atoms \( W \) turns out to be very weak and it can be handled more easily than the full potential. This net effect of the additive potentials of the ion core upon the valence electrons is often treated as a weak effective potential and is known as "the pseudopotential" in broad sense. By this weak pseudopotential term, any solid can be looked upon as an electron gas weakly perturbed by the pseudopotential. Such model applies reasonably accurately to the case of simple metals. More importantly, such pseudopotential is often found to have rapid convergence in a plane wave basis set, and this feature can be utilized proficiently for describing most of the semiconductors as well as metals with no d and f bands in the valence region.

The pseudopotential has several interesting properties [6]. It is non-local in that it is energy dependent and it depends on all ion positions and states. It is an operator and is not restricted to multiplying the wave function. Its form is not unique and the pseudowavefunctions are also not unique. That is an arbitrary linear combination of core states can be added to the pseudowavefunctions and they still remain solution of the same Schrödinger equation. Also, Harrison [6] showed that \( (E - E_{t,j}) \) may be represented by any function of the energies and the core states \( f(E,t,j) \) and the solution will remain unchanged. There exist many valid forms that will yield correct energies and wave functions. Given that \( W \) is small, we may use perturbation theory to solve for the electron energies. We note here that, even though the \( W \) form is arbitrary, if
the problem were solved exactly (i.e. to all orders in \( W \)), the correct solution would always be obtained. However, using perturbation theory, the \( W \) form will affect the result and the validity of the form used must be determined by the results obtained when applied to a specific problem.

In the equation (2.18) for the general expression of pseudopotential, \( V(r) \) contains the potential due to the cores, which may be written as a sum of potentials associated with the individual ions at position \( r_j \) and these are spherically symmetric:

\[
V_i(r) = \sum_j v_i(r - r_j) \quad (2.19)
\]

We have already written the core states as,

\[
| t, j > = \psi_t (r-r_j) \quad (2.20)
\]

If we require that the function \( f(E,t,j) \) depends only on the core states through the index \( t \), we may separate the pseudopotential and write it as a sum of contribution from individual ion sites as,

\[
W = \sum_j w(r-r_j) \quad (2.21)
\]

This assumption is essential to the pseudopotential matrix element calculation.

Choosing \( W \) of equation (2.21) as our pseudopotential allows factoring out the structure dependent term. We write
< k+q | W | k > = \Omega^{-1} \int \exp[-i(k+q).r] \cdot \Sigma_j w(r-r_j) \exp(ik.r) \, d^3r . \quad (2.22)

Changing the summation and integration order and factoring out \exp(-iq.r),

< k+q | W | k > = \Omega^{-1} \Sigma_j \exp(-q.r_j) \cdot \int \exp[-i(k+q).(r-r_j)] \cdot w(r-r_j) \exp[ik.(r-r_j)] \, d^3r . \quad (2.23)

The integral is just the integration of an individual potential with respect to the position of that particular ion and the sum contains the information about the system structure. So it is most convenient to write the pseudopotential matrix element in the form

< k+q | W | k > = S(q) < k+q | w | k > , \quad (2.24)

with

S(q) = 1/N \Sigma_j \exp(-iq.r) \quad (2.25)

≡ structure factor

and

<k+q|w|k> = \frac{1}{\Omega_o} \int \exp[-i(k+q).r] \cdot w(r) \exp[iq.r] \, d^3r \quad (2.26)

≡ form factor

where \Omega_o = atomic volume = \Omega/N
This factoring in the form factor and structure factor is critical to the development of the pseudopotential method. It allows simple solution of the seemingly intractable many-body problem.

The ionic potential details enter only through the form factor. If the potential operator $w$ is merely a multiplication operator, form factor depends solely on $q$ and is called *local pseudopotential*. On the other hand if potential operator $w$ depends both on $q$ and $k$ then it is called *non-local pseudopotential*.

The detailed ion positions enter only through the structure factor $S(q)$. The structure factor is a geometrical factor which can be constructed by the arrangement of ions in case of liquids and the arrangement of atoms in case of solid. The analysis of this factor for liquids as well as solids is different [6,11,12].

### 2.2 THEORY OF SCREENING:

In studying metallic properties which depends on electron-electron interactions a degenerate electron gas with a uniform neutralizing background has been used as a model for real metals. A precise knowledge of the dielectric function of an electron gas is necessary for the investigation of electron correlations. The random phase approximation (RPA) which has been extensively used in the literature provides a good description of the long wavelength excitation, but its validity is limited to high densities of electrons. The pair correlation function given by RPA shows an unphysical short-rang behaviour in the range of metallic densities. This is to be expected because we cannot expect the Hartree approximation to be a good description for interparticle correlations at distances much shorter than the average distance between electrons.
Several authors [28,35,36] have attended to take account of correlation and exchange corrections to the RPA dielectric function by the perturbation theory. The variational approaches [37,38] have also been employed to deal with strong correlations. A treatment of the short-range correlations has been presented by Hubbard [28], Singwi and his coworker [29,39,40], and Yasuhara [41]. Ichimaru and Utsumi [31] have reported dielectric formulation of strongly coupled electron liquid at metallic density.

The basic formulation for the dielectric function and how effects of the exchange and correlation are introduced in the screening functions are discussed in this article.

In the construction of the local pseudopotential, it is assumed that \( W \) covers three major effects [8],

\[
W = W_B + W_S + W_X ,
\]

where,

(i) \( W_B \) is the bare-ion local pseudopotential, the local potential by which the electrons interact with ions,

(ii) \( W_S \) is the Hartree screening contribution, which includes only the Coulomb interactions with the other conduction electrons determined self-consistently [6] and,

(iii) \( W_X \) contains contributions due to exchange and correlation.

\( W_B \) will be chosen later on as an appropriate model potential. \( W_S \) is
determined accurately while $W_x$ must be approximated.

Within the adiabatic approximation, we treat the conduction electrons as though responding in an electrostatic sense to the total potential $W$. The self-consistent electron contribution, $W_S$, due to the resulting charge density $\mathcal{S}(r)$ may be calculated using Poisson's equation [8]

$$\nabla^2 W_S(r) = -4\pi e^2 \mathcal{S}(r) \quad (2.28)$$

Considering Fourier analysis of the potential and density, we have

$$W_S(q) = \left(4\pi e^2 / q^2\right) \mathcal{S}(q) \quad (2.29)$$

So to calculate the screening contribution we must calculate the charge density, remembering that we are calculating the electron energies to second-order and the wavefunctions to first-order in perturbation theory. The charge density is given by [6,8],

$$\mathcal{S}(r) = \sum_k n_k \psi^*_k \psi_k \quad (2.30)$$

where the sum is over all electron states and $n_k$ is the occupation number, which is one when the state is occupied and zero when unoccupied.

Now using the expression

$$\psi_k = | k > + \sum_q a_{qk} | k+q > \quad (2.31)$$
with

\[ a_{qk} = \langle k+q \mid \hat{W} \mid k \rangle / [ E_k - E_{k+q} ]; \quad q \neq 0 . \]  

(2.32)

We calculate, keeping only first-order term

\[ \Psi_k^* \Psi_k = \Omega^{-1} \left[ 1 + \Sigma_q (a_{-qk}^* + a_{qk}) \exp(iq.r) \right]. \]  

(2.33)

We identify the Fourier coefficient, \( \mathcal{S}(q) \), defined by

\[ \mathcal{S}(r) = \Sigma_k \mathcal{S}(q) \exp(iq.r) \]  

(2.34)

as

\[ \mathcal{S}(0) = \Omega^{-1} \Sigma n_k = \Omega^{-1} N Z = \Omega^{-1} Z, \quad q = 0 \]  

(2.35)

\[ \mathcal{S}(q) = 2 \Omega^{-1} \Sigma n_k a_{qk}^*, \quad q \neq 0 . \]  

(2.36)

Substituting the values for \( a_{qk} \), yields

\[ \mathcal{S}(q) = 2 \Omega^{-1} \Sigma n_k w_q / [ E_k - E_{k+q} ] \]

\[ = \frac{m}{\hbar^2 \pi^3} \int \frac{d^3k}{k^2 - |k+q|^2}, \]  

(2.37)

where we have used the density in wave-number space with a factor 2 for spin to convert the sum to an integral and the zero order electron energy \( E_k = \frac{\hbar^2 k^2}{2m} \). The integral is evaluated over the Fermi sphere as,
\[ \int \frac{d^3k}{k^2 - |k+q|^2} = -\frac{\pi^2 k_F^2 \hbar^2 y^2}{m e^2} \left[ \epsilon(q) - 1 \right], \quad (2.38) \]

where

\[ \left[ \epsilon(q) - 1 \right] = \frac{m e^2}{2\pi k_F \hbar^2 y^2} \left( \frac{1 - y^2}{2y} \ln \frac{1+y}{1-y} + 1 \right), \quad (2.39) \]

and

\[ y = q/2k_F \]

so equation (2.37) results into

\[ g(q) = \frac{q^3 W}{4\pi e^2} \left[ 1 - \epsilon_H(q) \right], \quad (2.40) \]

where \( \epsilon_H(q) \) is the static Hartree dielectric function [6,8].

Substituting into equation (2.29), we find the result for the Fourier coefficients of \( W_S \) is

\[ W_S(q) = W(q) \left[ 1 - \epsilon_H(q) \right], \quad (2.41) \]

Momentarily, we are neglecting \( W_X \) of equation (2.27), so

\[ W(q) = W_B(q) + W_S(q), \quad (2.42) \]

and we see that
\[ W(q) = \frac{W_B(q)}{\varepsilon_H(q)} \quad (2.43) \]

so that the \( \varepsilon_H(q) \) plays the role of the dielectric function [8].

Now to incorporate the exchange and correlation effects in the screening calculation, we assume that there exists an average interaction \( I(q) \) within the electron gas,

\[ W_X(q) = I(q) \, \varepsilon(q) \quad (2.44) \]

Then using equation (2.29),

\[ W_S(q) + W_X(q) = \left( \frac{4\pi e^2}{q^2} \right) \varepsilon(q) + I(q) \, \varepsilon(q) \]

\[ = \left( \frac{4\pi e^2}{q^2} \right) [1 - f(q)] \, \varepsilon(q) , \quad (2.45) \]

where

\[ f(q) = \left( \frac{-q^2}{4\pi e^2} \right) I(q) , \quad (2.46) \]

and we parallel the screening calculation algebra to obtain

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

\[ = \frac{W_B(q)}{\varepsilon(q)} . \quad (2.47) \]

Thus the modified dielectric function \( \varepsilon(q) \) is given as,
$$\varepsilon(q) = 1 + [\varepsilon_H(q) - 1] [1 - f(q)] , \quad (2.48)$$

which incorporates the exchange and correlation effects in the screening through the local field correction function $f(q)$.

The static electron gas dielectric function $\varepsilon(q)$ is a quantity that is central to calculations of various properties of metals based on a perturbation technique. It describes the way in which the conduction electrons in a metallic system respond to zero-frequency external perturbations and an accurate representation of this function is an essential requirement for the calculation of most fundamental properties of a metal.

The role of the dielectric screening is very important in the case of various simple metals because the effect of electron gas cancels the pure coulomb repulsion between the ions to a much greater degree. Also if only the pure Coulomb potential (i.e. bare-ion) is considered, it always produces the bound states and the perturbation expansion will therefore be divergent. The screening is more important at small $q$. After the Fourier transformation to real space, small $q$ corresponds to large $r$, i.e screening removes the long-rang nature of the Coulomb potential while leaving its short-rang behavior (large $q$, $w(q) \propto q^2$) unchanged.

Various forms of local field correction function $f(q)$ [6,27-31,35,36,40,42-47] considered in earlier studies have been summarized in Table 2.1. Taylor and his coworker have noted that the actual form of any pseudopotential is much more sensitive to the choice of the electron gas dielectric function [30,48,49]. We avoid, here, the repetition of the discussion about all the dielectric functions, as they are already described in the respective articles. The validity and accuracy of all these dielectric
Table 2.1: Various forms of the local-field correction function $f(q)$.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$f(q)$</th>
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<tbody>
<tr>
<td>1 Hatree (RPA) [6]</td>
<td>0</td>
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<tr>
<td>2 Harrison [6]</td>
<td>$(1/2)\left[q^2/(q^2+4k_F^2/3)\right]$</td>
</tr>
<tr>
<td>3 Hubbard-Sham [28]</td>
<td>$q^2/[2(q^2 + \xi k_F^2)]$</td>
</tr>
<tr>
<td>4 Shaw [27]</td>
<td>$1 - \exp(-2.14q^2)$</td>
</tr>
<tr>
<td>5 Hubbard-Sham-Geldert-Vosko [42]</td>
<td>$q^2/[2(q^2 + \xi q^2)]$</td>
</tr>
<tr>
<td>6 Kleinman-Langreth [35]</td>
<td>$(1/4)\left[(q^2/(q^2+k_S^2+k_F^2) + q^2/(k_S^2+k_F^2))\right]$</td>
</tr>
<tr>
<td></td>
<td>with $k_S^2 = 2k_F^2/\pi\sigma_0$</td>
</tr>
<tr>
<td>7 Shaw-Pynn [43]</td>
<td>$(1/2)\left[1-\exp(-q^2/8k_F^2)\right] + (rq^2/k_F^3)\exp(-\alpha q^2/rk_F)$</td>
</tr>
<tr>
<td>8 Singwi-Sjolander-Tosi-Land [40]</td>
<td>$4A[1-\exp(-Bq^2/k_F^2)]$</td>
</tr>
<tr>
<td>9 Toigo-Woodruff [36]</td>
<td>Numerical Table</td>
</tr>
<tr>
<td>10 King-Cutler [44]</td>
<td>$q^2/[2(q^2+2k_F^2)]$</td>
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<tr>
<td>11 Mahanti-Das [45]</td>
<td>$\frac{1}{2}\left[\frac{q^2}{k_F^2}\left(\frac{1}{Z^2}+1\right) + \frac{q^2}{q^2+k_F^2}\left(\frac{1}{Z^2}+1\right)\right]$</td>
</tr>
<tr>
<td>12 Overhauser [46]</td>
<td>$0.275x^2/[1+2.5x^2+0.09375x^4]^{1/2}$</td>
</tr>
<tr>
<td>13 Vashishta-Singwi[29]</td>
<td>$A[1-\exp(-Bq^2/k_F^2)]$</td>
</tr>
<tr>
<td>14 Taylor [30]</td>
<td>$(q^2/4k_F^2)[1+0.1534/\pi k_F]$</td>
</tr>
<tr>
<td>15 Srivastava [47]</td>
<td>$(1/2)[1-\exp(-q^2/(q^2+\frac{1}{Z}k_F^2))]$</td>
</tr>
<tr>
<td>16 Ichimaru-Utsumi [31]</td>
<td>$AQ^4+BQ^2+C+[AQ^4+(B+8A/3)Q^2-C]\ln\left</td>
</tr>
</tbody>
</table>

- For more detail, see respective references.
functions can be judged from the fact that in which calculations they are used with a particular form of the pseudopotential.

Among all these dielectric functions the screening function proposed by Ichimaru and Utsumi [31] may be regarded as a latest and best choice due to following reasons: (i) The fitting formula for the local field correction is $r_s$ (electron gas sphere radius) dependent only. (ii) This function satisfies the self-consistency conditions in the compressibility sum rule and short-rang conditions. (iii) It also reproduces accurately the Monte-Carlo results as well as those of microscopic calculations. Hence, one must try any local form of the pseudopotential along with the screening function of Ichimaru and Utsumi [31] for making comprehensive study of metals. This can lead to some meaningful conclusions rather than academic exercise.

More details about the use of screening functions and applications of pseudopotential are given in the following chapters.