Chapter 2

Construction of Model Potential for Transition Metals and Historical Survey

2.1 Construction of Model Potential

As mentioned in Chapter 1, one of the methods used to calculate various metallic properties is the pseudopotential theory. To construct a local model potential for d-band metals, we consider Harrison's generalized OPW pseudopotential method to extend it to the study of properties of the d-band metals [Harrison (1969)]. In this method a generalized pseudopotential equation is derived similar to the case of simple metals so that the resulting plane wave matrix element of the pseudopotential may be written in the form:

$$
\langle \mathbf{k} + \mathbf{q} | W | \mathbf{k} \rangle = S(\mathbf{q}) \langle \mathbf{k} + \mathbf{q} | \omega | \mathbf{k} \rangle
$$

(2.1)

Here $W$ is the crystal pseudopotential and $\omega$ is the single ion pseudopotential. $S(\mathbf{q})$ is the structure factor given by

$$
S(\mathbf{q}) = N^{-1} \sum_i e^{-i\mathbf{q} \cdot \mathbf{R}_i}
$$

(2.2)

$N$ is total number of ions and $\mathbf{R}_i$ are the position vectors of ions. For a perfect lattice

$$
S(\mathbf{q}) = S_{\mathbf{q},\mathbf{q}_n}
$$

(2.3)
Harrison constructed the OPW (Orthogonalized Plane Wave) form factors for $d$-band metals. In fact, the pseudopotential idea could have been introduced in its present day form as far back as 1940 when OPW method was proposed as a tool for band theory studies [Herring (1940)]. This, however, was done by Phillips and Kleinman [1959] only. It became clear fairly soon that the OPW pseudopotential method was not useful for the transition metals. Ziman (1965) modified the Korringa-Kohn-Rostoker (KKR) method which is the Green's function method adapted for band structure calculations and Heine (1967) employed this modification (the KKRZ method) to construct the model Hamiltonian. Some time later, Hubbard [Hubbard (1967), Hubbard and Dalton (1968), Hubbard (1969)] discussed the basic principles underlying the model Hamiltonian approach within the scattering theory framework. Harrison [1969] introduced the transition metal pseudopotential.

To understand Harrison's approach, we start with one electron Schrödinger equation for a transition metal:

$$\hat{H} | \psi_k \rangle = E_k | \psi_k \rangle \quad (2.4)$$

In atomic unit system,

$$\hat{H} = -\nabla^2 + V(r) \quad (2.5)$$

$V(r)$ is one electron potential energy in the crystal.

The transition metals are characterized by having quasi-discrete $d$ states. Then, in constructing an OPW pseudopotential, it is necessary that the set of trial functions should contain both the types of states.

where $\tilde{Q}_n$'s are reciprocal lattice vector.
The function \( |\psi_\kappa\rangle \) must then be written
\[
|\psi_\kappa\rangle = \sum_n B_n | \vec{k} + \vec{Q}_n > + \sum_\alpha A_\alpha | \alpha > + \sum_d C_\alpha | d >
\] (2.6)

The set \( | \vec{k} + \vec{Q}_n > \) being a complete one, the above expansion is said to be in an over complete set. \( | \alpha > \) are the deeply bound core states. The first term corresponds to the nearly free electron (NFE) plane wave expansion. In the last term \( | d > \) represents quasi-localized \( d \) state. The core orbitals \( | \alpha > \) can be represented by free atom core functions. The crystal potential will move the corresponding levels (the core shift) but leave the wave functions themselves unaltered. In principle, the computational accuracy may be improved by taking these functions in Bloch LCAO combinations. This is the approach actually employed in OPW band calculations using a secular determinant [Woodruff (1957), Reser and Shirokovskii (1971)].

Throughout the following, \( | \alpha > \)'s are assumed to be the eigenfunctions of the crystal Hamiltonian, because on forming the crystal the core region remains unaltered. This implies that the core functions of neighbouring atoms must not overlap.

As for the \( | d > \) functions, we may choose the atomic \( d \) orbitals to model them but, since transition-metal \( d \) electrons are delocalized, these functions cannot be considered to be eigenfunctions of the crystal Hamiltonian because the potential affecting the \( d \)-electrons differs from the atomic potential. To take this difference into account, we suppose that the crystal potential \( V(r) \) may be related to the atomic potential by
\[
V(r) = V^{at}(r) - \delta V
\] (2.7)

It is clear that the effect of the crystal Hamiltonian on the \( d \) states may always be written as
\[
[-\nabla^2 + V(r)] | d >= (\epsilon_d - \Delta) | d >
\] (2.8)
where we have separated out an $r$ independent parameter $\epsilon_d$ and introduced an operator $\Delta$.

Operating on (2.8) by $<d|$ and using (2.7) gives

$$\epsilon_d = E_{d}^{\text{at}} - <d|\delta V|d> + <d|\Delta|d>$$

(2.9)

where $E_{d}^{\text{at}}$ is the atomic $d$ energy. For the core states $|\alpha>$ the operator $\Delta$ is, by definition, zero and they satisfy (2.9) with $d$ replaced by $\alpha$.

We assume that the crystal potential is spherically symmetric in the localization region of $d$ functions i.e. $d$ functions with different magnetic quantum numbers do not hybridize. Mathematically,

$$<d'|-\nabla^2 + V(r)|d> = \epsilon_d \delta_{dd'}$$

(2.10)

Clearly,

$$<d'|d> = \delta_{dd'}$$

From Eq. (2.8), we have

$$<d'|\Delta|d> = 0$$

(2.11)

Now we turn to pseudopotential itself. By analogy with simple metal pseudopotential theory we introduce a smooth function $\phi$, often referred to as “pseudowave function”. The true wave function is given by (2.6), while $b$ is given by its first term. That is,

$$|\phi> = \sum_n B_n (\vec{k} + \vec{Q}_n)$$

(2.12)

Substitution of (2.6) in Schrödinger equation (2.4) gives

$$[-\nabla^2 + V(r)]|\phi> + \sum_{\alpha} A_{\alpha} (E_{\alpha} - E_k) |\alpha> + \sum_d C_d (\epsilon_d - E_k) |d> - \sum_d C_d \Delta |d> = E_k |\phi>$$

(2.13)
To evaluate the coefficients $A_{\alpha}$, we multiply Eq. (2.13) by $< \alpha |$ to obtain

$$E_\alpha < \alpha | \phi > + A_\alpha (E_\alpha - E_k) - \sum_d C_d < \alpha | \Delta | d > = E_k < \alpha | \phi >$$

where the Hermitian property of Hamiltonian and the strong localization of $| \alpha >$ have been used in the first term.

Harrison assumed $\Delta$ to be constant in the core region. This is of course an approximation on the shape of the screening potential, it considerably simplifies the formalism and is quite in the spirit of Muffin Tin (MT) scheme of band structure calculations. The resulting expression for $A_\alpha$ is

$$A_\alpha = - < \alpha | \phi >$$

(2.14)

In order to evaluate $C_d$ we multiply Eq. (2.13) by $< d |$. The calculation of the first term requires the assumption of strong $d$ orbital localization, otherwise a boundary correction term will appear. This assumption also implies that $d$-functions of neighbouring atoms do not overlap i.e. $d$-bands are only formed by the perturbation potential $\delta V$ acting through the operator $\Delta$. The result is

$$C_d = - < d | \phi > + \frac{< d | \Delta | \phi >}{\epsilon_d - E_k}$$

(2.15)

Using eqs. (2.14) and (2.15) in Eq. (2.13), one gets

$$(-\nabla^2 + \hat{W} + \hat{W}_I - E_k) | \phi >= 0$$

(2.16)

$\hat{W}$ is simple metal pseudopotential, given by

$$\hat{W} = V(r) - \sum_{\alpha} (E_\alpha - E_k) | \alpha > < \alpha | - \sum_{\epsilon_d} (\epsilon_d - E_k) | d > < d |$$

$$+ \sum_d (| d > < d | \Delta) + \sum_d \Delta | d > < d |$$

(2.17)

$$\hat{W}_I = - \sum_d \frac{\Delta | d > < d | \Delta}{\epsilon_d - E_k}$$

(2.18)
Considering $|d\rangle$ states in Eq. (2.17) as core states and therefore taking $\Delta = 0$, we arrive at expression for the form factor of a $d$-band metals:

$$<\tilde{k} + \tilde{q} \mid W \mid \tilde{k}> = <\tilde{k} + \tilde{q} \mid V(r) \mid \tilde{k}>$$

$$-\sum_\alpha (E_\alpha - E_k) <\tilde{k} + \tilde{q} \mid \alpha > <\alpha \mid \tilde{k}>$$

$$-\sum_d \frac{<\tilde{k} + \tilde{q} \mid \Delta_d \rangle \langle \Delta_d \mid \tilde{k}>}{\epsilon_d - E_k}$$

(2.19)

Note that summation over $d$ contains atomic $d$ states which have been supposed to be localized. The last term of the above equation contains a matrix element between the functions $|k\rangle$ and $|d\rangle$. This term is often called hybridization potential. Eq. (2.19) can be used to calculate the total energy of a metal whose resonance energy is far away from $E_k$.

Apart from Harrison’s work there are a number of other related works, in particular, those by Moriarity [1970, 1972a,b,c, 1973, 1974, 1977, 1979] on heavy alkali and noble and alkaline earth metals. All of them, however, also treat the $d$ orbitals as a separate group, an approach which automatically brings about the same resonance form and so leaves one within the Harrison’s scheme. Thus Eq. (2.19) can be used to construct a local pseudopotential for noble, heavy alkali and alkaline earth metals.

Although Moriarity had been able to apply Harrison’s approach in the calculations of cohesive energies, form factors, phonon frequencies, electrical resistivities of full $d$-band and empty $d$-band metals, this method is highly rigorous and extremely intricate in its applications. However, local model potentials are of simple nature and can readily be applied in the calculations of large number of properties. This is why analogous to simple metals, the theoretical workers have adopted, on one hand, the different forms of local model potentials for $d$-band metals and, on the other hand, an effort has been made to include some features of Harrison’s approach in model potentials. These various potentials possess in common, $r$-space.
region accounting for the influence of $d$-electrons in between the rigidly bound core electrons in terms of Wigner-Seitz radius $R_d$. In the present thesis we construct the local pseudopotential from Eq. (2.19) as follows:

The first two terms of Eq. (2.19) represent simple metal pseudopotential. We choose to represent them the empty core model of Aschroft (1966). The third term can be approximated by using 3rd hydrogenic wave function. Considering $\Delta$ as a parameter, we require to find the $q$ dependence of $\langle \mathbf{k} + q | d \rangle$.

$$
\langle \mathbf{k} + q | d \rangle = \frac{1}{\Omega_o} \int \frac{\sin \pi \beta r^2 e^{-r/r_d} 4\pi r^2 dr}{[1 + (qr_d)^2]^q} 
$$

(2.20)

$r_c$ is core radius where $\Omega_o$ is atomic volume. $\beta$ is a parameter and $r_d$ represents in some sense the radius of $d$-orbital. $r_d$ is also treated as parameter.

Thus the pseudopotential which we propose to use for $d$-band metals has the following form:

$$
v_{\text{ion}}(q) = \frac{1}{\Omega_o} \left[ \frac{4\pi Ze^2}{q^2} \cos qr_c + \frac{\beta}{[1 + (qr_d)^2]^q} \right] 
$$

(2.21)

It should be noted that Lal et al. [1975] had similarly constructed a pseudopotential with four parameters.

$$
v_{\text{ion}}(q) = \frac{1}{\Omega_o} \left[ \frac{4\pi Ze^2}{q^2} + \frac{\beta_a}{[1 + (qr_c)^2]^2} + \frac{\beta_d}{[1 + (qr_d)^2]^q} \right] 
$$

(2.22)

These authors arbitrarily replaced the last term of Eq. (2.22) by $-\frac{Ze^2}{r_{c+d}} + \beta_3(r) = \text{const.}$ in the real space. Here $r_{c+d}$ is the core radius of $d$ electrons. We prefer the use of last term of Eq. (2.22) as it is. This means that we are not using any phenomenology in the $r$-space.

A pseudopotential form factor based on R-matrix approach [Hubbard (1967),...
Wu and Ohmura (1962), Burke and Robb (1975) can be written as
\[
\langle \vec{k} + \vec{q} | W | \vec{k} \rangle = \langle \vec{k} + \vec{q} | V | \vec{k} \rangle - \sum_{\alpha} \frac{< \vec{k} + \vec{q} | V | \alpha > < \alpha | V | \vec{k} >}{E_{\alpha} - E} \tag{2.23}
\]
Here \( W \) and \( V \) refer to pseudo and real crystal potentials. For transition metals \( \sum_{\alpha} \) includes the sum over \( d \) states also when original potential contains both deep and quasi-discrete levels. Assuming \( V \) to be constant in the core region the last term for \( d \) electrons can be approximated by the last term in Eq. (2.21). We note that in the OPW framework we have assumed \( \Delta \) constant while in \( R \)-matrix framework we assume \( V \) to be constant in the core region. These approximations may impose some burden on potential parameters and consequently some difficulty in the numerical results. Therefore, it is necessary to consider other essential features of the metals at hand in the numerical calculations.

In order to calculate the static and dynamic properties of transition metals, Moriarty (1970, 1972a,b, 1982, 1988) has included the overlap interaction \( \phi^r (R_i - R_j) \) for the nearest neighbour ion sites:
\[
\phi^r(r) = \alpha_1 \left\{ 1 + \alpha_2 \left( \frac{r}{R_{nn}} - 1 \right) + \alpha_3 \alpha_2 \left( \frac{r}{R_{nn}} - 1 \right)^2 \right\} \times \exp \left( -\alpha_4 \left( \frac{r}{R_{nn}} - 1 \right) \right) \tag{2.24}
\]
Here \( \alpha \)'s are the parameters.

Animalu (1973), while calculating phonon spectra of transition metals, has neglected the overlap interactions. He argued that the size of an ion (for given \( Z \)) is measured by the ratio \( \left( \frac{R_e}{R_a} \right)^3 = 2\alpha_{eff} \) where \( R_e \) is the empirical Pauling radius of the ion and \( R_a \) is radius of the atomic sphere. \( \alpha_{eff} \) is a parameter appearing in effective charge of the ion. This ratio for most of the transition metals is not more than 20%. But same is not true for \( Cu \), \( Ag \) and \( Au \). Thus, for noble metals the neglection of interatomic respulsive potential is not justified.
Onwuagba (1984) has investigated the role of attractive short range potential associated via $s - d$ interaction, with local field corrections in the lattice dynamics of transition metals. The possibility of representing the local field correction associated with $s - d$ interaction as an attractive short range interatomic potential having the same functional form in real space as the Born-Mayer repulsion due to overlap of wavefunctions of core electrons centred on the neighbouring ions was suggested by symmetry considerations and the patterns of the earlier numerical calculations by Oli and Animalu (1976).

As it is well known [Ehrenreich and Cohen (1959), Alder (1962), Wiser (1963)], local field effects are associated with the screening action of bound or virtual bound electrons in crystalline materials. In the lattice dynamics of transition metals characterized by the virtual bound nature of their $d$-electrons, the local field effects appear as non-vanishing off-diagonal components of the inverse dielectric matrix $\epsilon^{-1}(\vec{Q},\vec{Q}')$ which determines the linear response of the conduction electrons to a periodic crystal potential in a metal. Accordingly, the local field effects come into play in the dynamical matrix for phonon dispersion via electron-phonon interaction, or what is the same thing, the interaction between the ions via the polarization field of the conduction electrons. Because of its complexity, various approximate procedures have been developed for incorporating the local field corrections in transition metals where these corrections are important [Prakash and Joshi (1970), Hanke (1973), Sinha et al. (1971), Bertoni et al. (1974)]. Onwuagba and Animalu (1981) have reported a semi-empirical evidence that local field correction due to $s - d$ interaction in the lattice
dynamics of vanadium may be simulated by an attractive short range potential of Born-Mayer type which tends to cancel or screen the usual repulsive Born-Mayer potential. Onwuagba also constructed such an attractive short range potential in d-band metals directly from first principles. Such study was recently extended to f-band metals also [Onwuagba (1987)].

A more correct treatment of d-electrons was achieved in the tight binding approach [Wills and Harrison (1983, 1984)] and in the embedded atom method [Daw and Backes (1984), Daw and Hatcher (1985)], the latter being formally based on local density functional theory. Nevertheless, the form of Friedel density of states used for d-electrons in Wills and Harrison approach [1983, 1984] is quite far from the actual electron energy distribution. The embedded atom model is also based on the empirical assumption that the total electron density in a metal is simply the superposition of atomic densities and also the embedded function is chosen quite arbitrarily. Tight binding method in Waber [1984] or Sutton et al. [1588] treatment seems to be the most reliable one but d-electron interactions calculated rather accurately determines only a part of the total energy which is, however, supposed to be responsible for the phonon anomalies. Thus, one must use an additional empirical form of short range interaction in order to obtain an agreement between calculated lattice properties and measured ones. Antonov et al. [1990a,b] have used a Born-Mayer type form for such interaction along with Heine-Aberankov form of pseudopotential. Nevertheless, for transition metal it becomes necessary to use the sophisticated pseudopotential of special form in order to obtain satisfactory results. In the present study, therefore, we have used eq. (2.21) for pseudopotential and a Born-Mayer type short range interaction.

Animalu (1973) had suggested extending the model potential idea [Heine
and Abrenkov (1964)] to d-band metals. But Dagens has shown that Animalu's resonant form of the model potential is not quite correct [Dagens (1976)]. Dagens applied his resonant model potential to calculate total energy of Copper, silver, gold and Calcium [1977]. The ionic model potential proposed by Dagens can be written as

\[ v_{\text{ion}}(E') = \omega_o(E') + \frac{u}{E' - \epsilon} \]  

(2.25)

where \( E' = E - E_o \) is the energy counted from the bottom, \( E_o \), of the valence band and \( \omega_o \) is a Heine-Abrenkov model [1964] potential and \( \frac{u}{E' - \epsilon} \) represents resonance part.

\[ u(q, k') = 4\pi A_d \gamma(k') \gamma(k) \sum_m Y_{2m}(k') Y_{2m}(k) \]

(2.26)

with \( \vec{k} = \vec{k} + \vec{q} \). \( u \) has finite range \( R_d \). \( \gamma(k) \) is given by

\[ \gamma(k) = \frac{j_2(kR_d)}{1 + (kR_d/x_0)^2} \]

(2.27)

\( x_0 \) is first zero of \( j_2(x) \). Since

\[ j_2(qR_d) = \left[ \frac{3}{(qR_d)^3} - \frac{1}{qR_d} \right] \sin(qR_d) - \frac{3}{(R_dq)^2} \cos(qR_d) \]

(2.28)

An approximate \( v_{\text{ion}}(q) \) based on this model can be written as \( v_{\text{ion}} = \text{simple metal model potential} + \text{A term containing some power of } 1 + (qR_d)^2 \text{ in the denominator of a constant.} \)

Thus, although quite roughly, the second term in Eq. (2.21) has some justification from resonant model potential of Dagens also.

In almost all the model potentials constructed for transition metals, second term of Eq. (2.21) has been considered phenomenologically. In most of the cases, this term has been replaced by an attractive potential between core radius \( r_c \) and d electron radius \( r_d \).
The first attempt to construct a local model potential for $d$-band metals after Harrison’s analysis (1969) was made by Borchi and De Gennaro [1970a,b]. They proposed the following formula for form factor:

$$v(q) = -\frac{4\pi Z^2 e^2}{\Omega_0 q^2 \epsilon(q)} \left\{ \cos(qr_2) + \frac{A}{q} [\sin(qr_2) - \sin(qr_1)] 
- (qr_2) \cos(qr_2) + (qr_1) \cos(qr_1) 
- \frac{V_0}{q} [\sin(qr_1) - (qr_1) \cos(qr_1)] \right\}$$  

(2.29)

$\Omega_0$ is the volume per ion, $\epsilon(q)$ is the Hartree dielectric function and $q$ is the momentum transfer. Eq. (2.29) is obtained from the use of a simple $r$-space potential of the following form

$$v_{ion}(r) = \begin{cases} 
V_0 & \text{for } 0 < r < r_1 \\
-A & \text{for } r_1 < r < r_2 \\
-\frac{Z^2 e^2}{r} & \text{for } r_2 < r 
\end{cases}$$  

(2.30)

$V_0$ and $A$ are positive constants. They represent the core (repulsive) potential in the region $0 < r < r_1$ and $s-d$ hybridization (attractive) potential in the region $r_1 < r < r_2$ respectively. $r_1$ and $r_2$ are the adjustable parameters. The repulsive term arises from tightly bound inner core states. On this basis a suitable value for $r_1$ was taken to be 1 a.u. This is of the correct order of magnitude for the radius of the core in the noble metals. The intricate $s-d$ mixing is approximated by means of a negative square well potential extending from core radius $r_1$ to ionic radius $r_2$. Although this may seem to be an over simplification, the calculated form factors show that this is a rather plausible approximation. Finally, as negligible overlap between the valence and the $d$-electrons may be assumed for $r > r_2$, a pure Coulomb potential is reasonably admitted outside the ionic radius. The parameters $A$ and $V_0$ were determined to fit the $s-p$ band gap at $L$ (the centre of the nearest zone face and to reproduce known resistivity of liquid metals.)

The second attempt to construct a local model potential was that of Lal et al. [1973, 1975]. This we have noted earlier in this chapter. Here we present a complete real space form of their potential.
(i) **Pseudo-core region** : $(r < r_{ps})$

There is a complete cancellation of potential in the same sense as in the empty core model. But $r_{ps}$ is less than Aschroft's core radius $r_c$.

(ii) **Effective d-electron region**: $(r_{ps} < r < r_{c+d})$

In this region, there is a superposition of Coulombic contribution $-\frac{Ze^2}{r}$ and the repulsive potential $B(r)$ (say) characterizing the third term of Eq. (2.22):

$$W(r) = -\frac{Ze^2}{r} + B(r) \quad (2.31)$$

The two terms in Eq. (2.31) tend to cancel each other. For the simplification of the model, they arbitrarily took

$$W(r) = -\frac{Z^*e^2}{r_{c+d}} \quad (2.32)$$

where $r_{c+d}$ defines the core radius including $d$-electrons. $Z^*$ denotes the effective ionic charge.

(iii) **Coulombic region**: $(r > r_{c+d})$:

In this region the potential is $-\frac{Ze^2}{r}$. These authors termed this potential as modified Aschroft's empty core models for $d$-band metals.

**Model Potential of Animalu**

Eq. (2.16) can be written as

$$(-\nabla^2 + \hat{W} + \hat{W}_t) | \phi \rangle = E_k | \phi \rangle \quad (2.33)$$

Here $\hat{W} + \hat{W}_t$ is an energy dependent non-local operator which is non-unique. Therefore, the calculation of its matrix elements is difficult in
practice. In most of the physical properties of metals, the electronic states in the vicinity of Fermi energy, $E_F$ contribute maximum. Therefore, attempts have been made to parameterize $(\hat{W} + \hat{W}_t)$ such that Eq. (2.33) maps out Fermi surface as exactly as possible.

$(\hat{W} + \hat{W}_t)$ is a periodic potential and it is sum of bare ion potentials $v_{\text{ion}}$ (electron-ion interaction) and the Hartree self-consistent potential $v_{\text{sc}}$

Heine and Abrenkov [1964] proposed one of the most general forms of model potential which is defined as

$$v_{\text{ion}}(\vec{r}, E) = -\sum_{\ell} A_\ell(E) P_\ell \quad \text{for } r < R_M$$

$$= -\frac{Z e^2}{r} \quad \text{for } r > R_M$$

Here $A_\ell(E)$ are the energy and angular momentum dependent well depth parameters and $P_\ell$s are the projection operators and $R_M$ is the model radius. Model potentials have also been given by Shaw [1968, 1969, 1970, 1972] and Rasolt and Taylor [1975].

Animalu [1973] extended the quantum defect method for transition metals and replaced $A_\ell(E) = \frac{Z e^2}{R_M}$ by $C$, a constant, for $\ell \geq 3$. With this, HA model potential for transition metal becomes

$$v_{\text{ion}}(\vec{r}, E) = -C - (A_0 - C) P_0 - (A_1 - C) P_1$$

$$- (A_2 - C) P_2 \quad \text{for } r \leq R_M$$

$$= -\frac{Z e^2}{r} \quad \text{for } r > R_M$$

Parameters $A_\ell(E)$ are obtained by solving the Schrödinger equation for model potential inside and outside the potential well and by matching the wave function and its derivatives at the potential well boundaries. The parameter $A_2(E)$ is found to be proportional to $(E_d - E)^{-1}$ and thus exhibits a resonant behaviour at $E = E_d$. Therefore, the last term of eq. (2.35) is
equivalent to $\tilde{W}_t$ of Eq. (2.33). This term can be regarded as an $s - d$ hybridization potential. Upadhyaya and Animalu [1977] have extended this approach to rare earth metals by assuming $A_\ell(E) = \frac{Ze^2}{R_M} = C$ for $\ell \geq 4$. With this approximation

$$v_{\text{ion}}(r, E) = \begin{cases} 
-C - (A_o - C) P_o - (A_1 - C) P_1 - (A_2 - C) P_2 \\ -(A_3 - C) P_3 & \text{for } R < R_M \\
-\frac{Ze^2}{r} & \text{for } r > R_M
\end{cases}$$

(2.36)

$A_3(E)$ is found to be proportional to $\frac{1}{\eta W_f} \frac{1}{(E_f - E)}$ where $E_f$ is the energy of $f$-state in the metal and $W_f$ is the width of the $f$-band resonance. Thus the last term of (2.36) exhibits resonance at $E = E_f$ and represents $s - f$ hybridization.

Moriarty [1972a,b] and Animalu [1973] studied the lattice dynamics of noble metals. Their theoretical results were, however, in poor agreement with the experimental measurements.

Noticing this fact Nand et al. [1975, 1976a, 1977, 1982] have proposed a transition metal model potential which includes in a simple parametric way all the features dictated by the physics of the situation. In noble metals, below the Fermi energy level there are filled $d$-bands which tend to push up the energy of a given state. The effect called "hybridization" would require a repulsive term in the model potential. Hence, in the $r$-space, inside the core radius $r_1$ the model potential is positive, while from the core radius $r_1$ to the ionic radius $r_2$ it is negative. Beyond the ionic radius, the model potential is Coulombic in nature.

$$v_{\text{ion}}(r) = \begin{cases} 
Ze^2 \left[ -\frac{1}{r_2} + \frac{\exp(r-r_1)/r_2}{r_2-r_1} \left(1 - \frac{r}{r_1}\right) \right] & r < r_2 \\
-\frac{Ze^2}{r} & r > r_2
\end{cases}$$

(2.37)

The value of core radius $(r_1)$ was taken to be 1 a.u. on the lines of Borchi
and De Gennaro [1970] while the values of ionic radii are 1.815 a.u. and 2.38 a.u. for Cu and Ag respectively. For Au, \( r_2 = 2.6 \) a.u.

In the \( q \)-space, the model potential takes the following form:

\[
v_{\text{ion}}(q) = -\frac{4\pi Ze^2}{\Omega_0 q^2} \left[ \frac{\sin qr_2}{qr_2} - \frac{4r_2^2 q^2 (q^2 r_2^2 - 1)}{(1+q^2 r_2^2)^3} \exp \left( \frac{r_1}{r_2} \right) \right] - \frac{r_2}{r_2-r_1} \exp \left[ \frac{rf}{(1+qr_2^2)^3} \right] \{8qr_2 \cos qr_2 \\
+ \sin qr_2 (3 - 6q^2 r_2^2 - q^4 r_2^4) \}
\]

Swaroop [1974] has also proposed the following form of model potential for simple metals.

\[
v_{\text{ion}}(q) = \frac{1}{\Omega_0} \left[ -\frac{4\pi Ze^2}{q^2} + \beta \exp \left( -q^2 R_c^2 \right) \right]
\]

This model potential was used by George et al. [1978] to study lattice dynamics of noble metals [see also George et al. (1976, 1978)].

It is interesting to note, here, that original Heine-Aberankov model potential was used by Nikulin and coworkers to study lattice dynamics of noble metals [Nikulin and Thishaskovskaya (1968)]. Singh and Prakash [1973] used Harrison point ion model potential [1966] together with a dielectric function calculated in the non-interacting band scheme [see also work by Singh and Prakash and Singh et al. (1973, 1975a, b, c, 1976)]. Kumar and Hemkar (1978) argued that \( d \)-states contribute substantially in determining the electronic properties of metals. For noble metals, these authors proposed the following model potential on the lines of Lal et al. [1975].

\[
v_{\text{ion}}(r) = \begin{cases} \frac{Ze^2 r_{ps}}{r_c+d(r_c+d-r_{ps})}, & r < r_{ps} \\ \frac{Ze^2}{r_{c+d}}, & r_{ps} < r < r_{c+d} \\ \frac{Ze^2}{r}, & r > r_{c+d} \end{cases}
\]

Here region \( r < r_{ps} \) is pseudocore region and \( r_{ps} < r_c \) (the core radius), region between \( r_{ps} \) and \( r_{c+d} \) is effective \( d \)-electron region. \( r_{c+d} \) defines core
radius including $d$-electrons and is taken equal to the ionic radius. In $q$-space the bare electron ion model potential assumes the form given by

$$v_{\text{ion}}(q) = -\frac{4\pi Z e^2}{\Omega_0 q^2} \left[ \frac{\sin q r_{e+d}}{q r_{e+d}} + \frac{r_{ps}}{r_{e+d} - r_{ps}} \left( \cos q r_{ps} - \frac{\sin q r_{ps}}{q r_{ps}} \right) \right]$$

(2.41)

where $r_{ps}=0.51 R_a Z^{-1/3}$

(2.42)

where $R_a$ is the atomic radius. The value of $R_a$ is determined by using the relation

$$\left( \frac{R_e}{R_a} \right)^3 = 2\alpha_{\text{eff}}$$

(2.43)

which measures quantitatively the size of the ion. $r_{e+d}$ was taken as $R_M$ of Animalu [1973].

Vrati et al. [1977, 1979] have proposed an optimized form of model potential for noble metals. In $r$-space there is no discontinuity in the model potential. In $q$-space the model potential is given by

$$v_{\text{ion}}(q) = -\frac{4\pi Z e^2 r_a^2}{\Omega_0} \left[ \frac{1}{q^2 r_a^2} + \frac{\exp(1)}{4 + q^2 r_a^2} - \frac{1 + \exp(1)}{1 + q^2 r_a^2} \right]$$

(2.44)

$r_a$ is taken equal to 1 a.u.

Yamada [1978, 1980a,b, 1981] proposed a model pseudopotential method to investigate band structure of noble and transition metals. This method is based on ideas of empirical pseudopotential method of Fong and Cohen [1970] and transition metal model potential of Animalu [1973]. The model potential is defined as

$$v(r) = v_L(r) + v_{NL}(r)$$

(2.45)

Here $v_L(r)$ and $V_{NL}(r)$ are the local and non-local parts of $v(r)$ respectively. The matrix element between plane waves $| \vec{K} + \vec{Q} \rangle$ and $| \vec{K} + \vec{G} \rangle$ can be written as

$$\langle \vec{K} + \vec{Q} | v(r) | \vec{K} + \vec{G} \rangle = \langle \vec{K} + \vec{Q} | v_L(r) | \vec{K} + \vec{G} \rangle / \epsilon(G) + \langle \vec{K} + \vec{Q} | v_{NL}(r) | \vec{K} + \vec{G} \rangle$$

(2.46)
where $\bar{Q}$ is reciprocal lattice vector, $|\bar{Q}| = |Q - \bar{Q}|$. The $v_{f}^{s}(r)$ and $v_{NL}^{(d)}(r) = v_{NL}(r)$ are defined as

$$v_{f}^{s}(r) = C + \{- (A_0 - C) P_0 - (A_1 - C) P_1\}_{FSA} \quad r < R_M$$

$$v_{NL}^{(d)} = -\frac{Ze^2}{r}$$

$$C = \frac{Z}{R_M}$$

and $FSA$ denotes on fermi surface approximation.

Khanna [1981a,b] has proposed a Wigner-Seitz radius dependent model potential. This model potential presents a variable nature in the inner region and becomes Coulombic beyond $r > \frac{R_a}{2}$. Although this model potential was proposed for simple metals, it was found to be somewhat useful for noble metals also. In the $q$-space the form of this model potential is:

$$v_{ion}(q) = \frac{4\pi Z e^2}{4\pi q^2} \left\{ - \cos \left( \frac{q_2}{2} \right) + q_s \sin \left( \frac{q_2}{2} \right) e^{-\frac{q_2}{2}} \right\}$$

$$r_s = \left( \frac{3m}{4\pi e^2} \right)^{\frac{1}{3}} = Z^{-\frac{1}{3}} R_a, \quad q_2 = q R_1 (R_1 = 1 a.u.)$$

Starkloff and Joannopolous [1977] have given a simple local pseudopotential formalism capable of describing $d$-band metals. The basic concept underlying this method is to include the outermost $s$ and $p$ core electrons in addition to the customary $d$ and $s$ valence electrons. The method thus provides a description of complete outer valence shell. Therefore, we need only deal with a local potential. Beginning with a self-consistent $X_0$ atomic potential [Herman and Skillman (1974), Slater (1974)] using local Slater $\rho_0^{1/3}$ exchange, the screening potential due to the outer shell electrons screening themselves is subtracted out. The resulting potential termed as base potential rapidly approaches the Coulomb potential of the respective ion outside of core although it still contains the effects of the mutual screening of the core and valence electrons. This base potential is then pseudized by multiplying it with a smooth step-like function

$$f (r, \lambda, r_c) = \frac{1 - e^{-\lambda r}}{1 + e^{-\lambda (r - r_c)}}$$

(2.50)
where $r_c$ is core radius and $\lambda$ is a reciprocal length characterizing the smoothness of the step function. This correction function sets the potential almost to zero inside the core radius but leaves the base potential essentially unchanged outside.

Khanna [1981a,b] has proposed a special form of model potential for noble metals:

$$v_{\text{ion}}(q) = \frac{4\pi Ze^2}{\Omega q^4} \left[ \cos qr_1 - \frac{\Omega}{r_1} (\sin q r_m - q r_m \cos q r_m) e^{-q r_m} + \frac{2}{r_1} (1 - \cos q r_m) \right]$$

(2.51)

$r_1 = 1$ a.u. and $r_m$ is obtained from band gap data at point $L$ in the Brillouin zone.

Kiejna [1980] has tested the validity of Krasko-Gurskii [1969a,b] model potential for noble metals. In the $r$-space this potential is

$$v_{\text{ion}}(r) = \frac{Z e^2}{r} \left( e^{-\frac{r}{r_c}} - 1 + \frac{q}{r_c} e^{-\frac{r}{r_c}} \right)$$

(2.52)

In the $q$-space:

$$v_{\text{ion}}(q) = \frac{4\pi Ze^2 (2a - 1) (qr_e)^2 - 1}{\Omega_0 q^2 \left[ (qr_e)^2 + 1 \right]^2}$$

(2.53)

Barua and Sinha [1978] calculated the form factor of gold using Harrison's modified point ion model with experimental elastic data and compared the same with the form factor obtained from Fermi surface data.

Kulshrestha et al. [1975, 1976] have proposed a model in which square well attractive potential of the Heine-Abrenkov type was replaced by a triangular one.

$$v_{\text{ion}}(r) = \begin{cases} \frac{-Ze^2 (r-r_1)}{r_m (r_m-r_1)} & \text{for } r < r_m \\ \frac{-Ze^2}{r} & \text{for } r > r_m \end{cases}$$

(2.54)

This potential is repulsive from $r = 0$ to $r = r_1$ (core radius) and attractive for $r > r_1$, whereas outside the ionic radius $r_m$, the potential is purely
Coulombic. As for the Borchi-DeGennaro potential, the repulsive part of this potential is due to the core overlap and the attractive part in the region \( r_1 < r < r_m \) is due to the \( s-d \) hybridization effects.

By assuming that the structure factors of \( Ag \) and \( Au \) would not differ much, Kulshreshtra et al. [1975, 1976] calculated the liquid metal resistivity of the latter. They argued from the results obtained that their potential needed to be made more negative in the region \( r_1 < r < r_m \) because the \( d \)-component of the electron wave function within a given atomic cell sees a strongly negative potential [Heine and Weaire (1970)]. This point was incorporated in the potential proposed by Upadhyaya and Sharma [1977], albeit at the expense of introducing one more adjustable parameter. Their model potential for the noble metals may be written as [see also Sharma (1978)]

\[
v_{\text{ion}}(r) = \begin{cases} \frac{R(r_c-r)}{r_c} & r < r_c \\ \frac{-2Ze^2}{r_m} & r_c < r < r_m \\ \frac{-2Ze^2}{r} & r \geq r_m \end{cases}
\]  

Eq. (2.55) in the \( q \)-space is given by

\[
v_{\text{ion}}(q) = \left(\frac{4\pi}{n_e q^2}\right) \left(q^2 (Ar_m - Ze^2) \cos qr_m\right) \\
- (Ar_c \cos qr_c) + \left(\frac{2A}{r_c} \sin qr_c\right) - A \sin qr_m + \left(\frac{2Ze^2}{r_m} \left(1 - \cos qr_c\right)\right)
\]

with

\[A = \frac{2Ze^2}{r_m}\]

where \( R, r_c \) (core radius) and \( r_m \) (ionic radius) are all parameters. They showed that their constant negative part in the region of \( s-d \) hybridization is more negative than that of Kulshreshtra.

Idress et al. [1982] proposed a phenomenological one parameter model pseudopotential for noble metals. This potential which contains the \( s-d \)
hybridization and core-core exchange contribution was analyzed in some detail and it was shown that its prediction on the liquid metal resistivity, thermoelectric power and the band gaps were in better agreement with the experiment than those of other model potentials considered in the literature. This potential is given by

\[ v_{\text{ion}}(r) = \begin{cases} \frac{Ze^2(r_m - r)R_W}{R_W(R_W - r_m)} & 0 < r < r_m \\ -\frac{Ze^2}{R_W} & r_m < r < R_W \\ -\frac{Ze^2}{r} & R_W < r \end{cases} \] (2.57)

This potential is repulsive from 0 to \( r = \frac{r_m}{R_W} \), attractive and constant in the region \( r = r_m \) to \( r = R_W = \left( \frac{3\pi^2}{4\varepsilon} \right)^{\frac{1}{3}} \) and purely Coulombic beyond.

In q-space (2.57) is given by

\[ v_{\text{ion}}(q) = \frac{4\pi}{\Omega q^3} \left[ (ARm^2 + B - ARW R_m) (\sin qR_m - qR_W \cos qR_m) \right. \]

\[ -B (\sin qR_W - qR_W \cos qR_W) - \frac{ARW}{q} \left( \frac{qR_m \sin qR_m}{2 (\cos qR_m - 1)} - \frac{Ze^2}{2} \cos qR_W \right) \] (2.58)

The most important physical quantity, in the theoretical study of phonon frequencies of transition and rare earth metals is the ion-ion interaction potential. There have been consistent efforts to find an empirical ion-ion potential for these metals. Harrison and coworkers [Wills and Harrison (1983), Harrison (1983, 1984), Harrison and Straub (1987)] made an attempt to obtain a general ion-ion potential for transition and rare earth metals. The expressions for the different contributions to the total energy

\[ E_T = E_{es} + E_{el} + E_{fe} + E_{bs} \] (2.59)

of a transition metal are written up to second order in \( \Delta \). It is found that the Coulomb terms cancel exactly. The remaining terms are calculated using atomic data such that the bulk properties are reproduced reasonably. From this total energy calculations, the ion-ion interaction potential is estimated
which is written as

\[ v_i(r) = v_{fe}(r) + v_{dd}(r) + v_d(r) \]  \hfill (2.30)

Here \( v_{fe}(r) \) is the effective two-body interaction between the ions screened by conduction electrons. If one uses Thomas-Fermi approximation for the screening and Aschroft empty core model potential for the bare ions, \( v_{fe}(r) \) is given by

\[ v_{fe}(r) = \frac{Z^2 e^2}{r} \cosh^2 \left( K_{TF} r_c \right) e^{-K_{TF} r_c} \frac{e^{-K_{TF} r}}{r} \]  \hfill (2.61)

where

\[ K_{TF} = \left( \frac{4K_F}{\pi a_0} \right)^{\frac{1}{2}} \]  \hfill (2.62)

is the Thomas-Fermi inverse screening length, \( r_c \) is the effective core radius and it is taken as the model potential parameter. \( a_0 \) is Bohr's radius.

The potential \( v_{dd}(r) \) arises due to broadening of \( d \)-states into the bands. The \( d \)-states on different ion sites are taken to be non-overlapping. However, \( d \)-states overlap through free electron states and the coupling between them is given by

\[ v_{dd'} = \sum_k \frac{\langle d | \Delta | \vec{k} \rangle \langle \vec{k} | \Delta | d' \rangle}{E_d - E_{\vec{k}}} \]  \hfill (2.63)

Using atomic \( d \)-state wave functions and summing over \( \vec{k}_j \) the inter-ionic separation dependence of \( v_{dd'}(r) \) is given as

\[ v_{ddm} = \frac{(\eta_{ddm}) \left( \hbar^2 r_d^3 \right)}{m r_d} \]  \hfill (2.64)

where \( r_d \) is the radius of \( d \)-state wavefunction and

\[ \eta_{ddm} = \frac{45}{\pi}, \frac{30}{\pi}, \frac{15}{2\pi} \]  \hfill (2.65)

for \( m = 0,1,2 \) respectively. Further, the effect of \( d \)-bands is included through rectangular model of density of \( d \)-band states as suggested by Friedel [1969]. Retaining only one centre integrals within the Friedel model
for the $d$-bands, the average $d-d$ overlap interaction is given by

$$V_{dd}(r) = -Z_d \left( 1 - \frac{Z_d}{10} \right) \left( \frac{12}{9} \right) \frac{281}{\pi} \frac{h^2 r_d^3}{m r^5}$$

(2.66)

where $n$ is the number of nearest neighbours.

There is also a contribution to the interionic potential due to $s-d$ hybridization between the occupied and unoccupied $d$-states and the free electron states $| k >$. The $s-d$ hybridization modifies the $d$-charge in the occupied $| d >$ states which gives a change in the $d$-state occupation number, say $\Delta Z_d$. This $\Delta Z_d$ is accompanied by an equal and opposite charge in the $s$-band charge $\Delta Z_s$ so as to keep the atom neutral. Wills and Harrison [1983] accounted for $s-d$ hybridization by modifying the values of $Z_s$ which have been calculated self-consistently by Pettifor [1977] and Moriarty [1982]. Since the $d$-states overlap through $| k >$ states, therefore, $| d >$ states are perturbed and are rendered non-orthogonal. An additional interaction arises due to overlap of perturbed $| d >$ states on the nearest neighbours. The first order calculations yield averaged overlap interaction as

$$V_d(r) = \frac{225.0 h^2 r_d^6}{\pi^2 m r^5}$$

(2.67)

$v_d(r)$ has the effect of shifting the $d$-band centre.

Hartree dielectric function $\epsilon(q)$ given by

$$\epsilon(q) = 1 + \frac{m e^2}{2 \pi K_F h^2 \eta^2} \left[ 1 + \frac{1 - \eta^2}{2 \eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \right]$$

(2.68)

with $\eta = \frac{q}{2K_F}$, exhibits logarithmic singularity at $q = 2K_F$. Therefore, it becomes almost impossible to evaluate analytically the band structure contribution to energy and phonon frequency. Singh et al. [1989, 1990] and
Singh and Singh [1989a,b,c] expressed $\epsilon^{-1}(q)$ by a rational function, proposed by Pettifor [1982, 1984] which is written as

$$
\epsilon^{-1}(q) = \sum_{n=1}^{6} D_n \frac{q^2}{q^2 - q_n^2}
$$

(2.69)

where the coefficients $D_n$ and the poles $q_n$ are determined by reproducing $\epsilon^{-1}(q)$ as exactly as possible except the logarithmic singularity. Use of this equation augments the free electron part of inter-ionic potential which can be obtained by taking the Fourier transform of $v_{\text{ion}}(q)\epsilon^{-1}(q)$.

Singh et al. [1989a,b,c, 1990a, 1992] also used the temperature dependent damping factor, in the interatomic interaction,

$$\exp \left( -\frac{\pi k_B T r}{\hbar v_F} \right)$$

where $k_B$ is Boltzmann constant, $T$ is temperature and $v_F$ is Fermi velocity. The anomalous structure in the phonon dispersion relations is not found in the calculations using rational dielectric function. The exchange and correlation interactions in the $d$-band metals are important and these should be included [Treglia et al. (1980)].

The most convenient way of introducing local field effects arising from $s-d$ interaction has been suggested by Onwuagba [1984] as mentioned earlier.

The total interaction potential energy of a system of ions with chemical valence $Z = Z_s + Z_d$ and system of $s$ and $d$ electrons can be written as

$$
\Phi(R_1, R_2, ..., R_N) = \sum_{i>j} \frac{Z_s^2}{|R_i - R_j|} + \int \sum_{i>j} \rho(r) \left( \mathbf{r} - \mathbf{R}_i \right) V \left( \mathbf{r} - \mathbf{R}_j \right) d^3r
$$

(2.70)

$$
= \Phi_o + \Phi_{ss} + \Phi_{dd} + \Phi_{sd} + \Phi_{ds}
$$

(2.71)
where

\[ \Phi_{nm} = \int \sum_{i>j} \rho_n (\vec{r} - \vec{R}_i) V_m (\vec{r} - \vec{R}_j) \, d^3 r \]

\[(n, m = s, d)\]  

(2.72)

Now writing the charge densities as 

\[ \rho_s (\vec{r} - \vec{R}) = Z_s \delta (\vec{r} - \vec{R}) \]

and

\[ \rho_d (\vec{r} - \vec{R}) = \sum_d \Psi_s (\vec{r} - \vec{R}) \Psi_d (\vec{r} - \vec{R}) \]  

and using Poisson's equation and the hydrogenic wave functions, Onwuagba [1984] showed that there is a sizeable attractive component of the interatomic potential due to the \( s - d \) interaction in transition metals, which has the same form as Born-Mayer potential.

Wang and Overhauser [1987a,b] have constructed, in the pseudopotential framework, a theory of phonon spectra in metals which combines the conventional pseudopotential methods with shell model of Dick and Overhauser [1958]. In this method an ion is divided into an outer core and a last-filled electron shell. The conduction electrons screen all of the following interactions: core-core, core-shell and shell-shell. An important feature of the theory is inclusion of exchange interactions of shell electrons with the conduction electron sea. As a consequence, three different dielectric functions appear in the theory appropriate to core-core, core-shell and shell-shell interaction energies. The pseudopotential of each ion has two parts: one for the core and one for the shell. The pseudo-ion core and shell charge densities can be appropriately modelled. The vibrations of cores and shells have different amplitudes. Only Coulomb interactions, screened by the conduction electron sea, enter the theory. The core and shell pseudopotentials involve just one parameter each and these are determined phenomenologically. These authors carried out highly successful calculations of lattice dynamics of \( Na, K, Rb, Cs, Ag, Au, Cu, Ca, Sr, Ba, Yb, Al \) and \( Pb \).

It should be noted that charge densities \( \rho_s \) and \( \rho_d \) have been modelled differently by Onwuagba [1984] and by Wang and Overhauser [1987a,b].
It is now well known that dielectric tensor for valence electron plays a vital role in the determination of physical properties of metals. The quantum mechanical description of dielectric tensor is given by many authors [Venkataraman et al. (1975), Sham and Ziman (1965), Sinha (1960)]. When electron-electron interaction is included in Hartree approximation and the linear response to the external field is accounted for, we get

\[ \epsilon (\vec{q} + \vec{Q}, \vec{q} + \vec{Q}') = \delta_{QQ'} - v (\vec{q} + \vec{Q}) \omega X^o (\vec{q} + \vec{Q}, \vec{q} + \vec{Q}') \]  

(2.73)

where

\[ X^o (\vec{q} + \vec{Q}), (\vec{q} + \vec{Q}') = \sum_{\vec{K}, \mu, \vec{K}', \mu'} \left[ \frac{f_{\vec{K} \mu} f_{\vec{K}' \mu'}}{\epsilon_{\vec{K} \mu} - \epsilon_{\vec{K}' \mu'}} \right] \times \]

\[ \frac{\langle \psi_{K'\mu'} | \psi_{K\mu} \rangle}{\langle \psi_{K'\mu'} | \psi_{K\mu} \rangle} \]

(2.74)

Here

\[ \vec{K}' = \vec{K} + \vec{Q} \pm \vec{\mu} \]  

(2.75)

and

\[ \vec{H} = \vec{q} \pm \vec{Q}' \]  

(2.76)

\[ v (\vec{q}) = \frac{4\pi e^2}{Q^2} \]  

(2.77)

\( \vec{K} \) is electron state wave vector and \( \mu \) denotes the band index (= \( \ell m \sigma; \ell, m, \sigma \) are orbital, magnetic and spin quantum numbers respectively).

A full quantum mechanical treatment of frequency and wave vector dependent dielectric matrix is given by Nozieres and Pines [1958, 1959] and by Ehrenrich and Cohen [1959].

Neglecting the off-diagonal elements and restricting the wave vector \( \vec{q} \) in
the first Brillouin zone, Eq. (2.72) simplifies as

\[ \epsilon(q, q) = 1 - \nu(q) \sum_{k_\mu k_\mu'} \left[ \frac{f_{k_\mu k_\mu'}}{E_{k_\mu} - E_{k_\mu'}} \right] \times |\langle \psi_{k_\mu} | e^{-iq\cdot r} | \psi_{k_\mu'} \rangle|^2 \]  

(2.78)

In the free electron approximation one gets

\[ \epsilon(q) = 1 + \frac{m e^2}{2\pi K_F h^2 \eta^2} \left[ 1 + \frac{1 - \eta^2}{2\eta} \ln \left| \frac{1 + \eta}{1 - \eta} \right| \right] \]  

(2.79)

with \( \eta = \frac{q}{2K_F} \). \( \epsilon(q) \) is well known Lindhard function.

The dielectric function given above is in the Hartree approximation. The electrons are assumed non-interacting and single particle wave functions are used. In reality, the electrons are interacting and many body interactions which are known as exchange and correlation interactions among the conduction electrons must be accounted for the calculation of \( \epsilon(q) \) [Nozieres and Pines (1958)]. This is a complete subject in itself, therefore, we directly write the modified form of dielectric function as follows:

\[ \epsilon(q) = 1 + [\epsilon_H(q) - 1] [1 - Y(q)] \]

The function \( Y(q) \) accounts for the exchange and correlation effects.

The exchange and correlation interactions have been investigated extensively for the free electron gas using many body perturbation theory. Various expressions for \( Y(q) \) have been suggested in the literature. We represent them in Table 2.1.
### Table 2.1

#### Different Forms of $Y(q)$

<table>
<thead>
<tr>
<th></th>
<th>Formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hartree (RPA) Cohen and Phillips</td>
</tr>
<tr>
<td>2</td>
<td>Harrison</td>
</tr>
<tr>
<td>3</td>
<td>Hubbard-Sham [1958, 1959]</td>
</tr>
<tr>
<td>4</td>
<td>Shaw [1967, 1968]</td>
</tr>
<tr>
<td>5</td>
<td>Geldart-Vasko [1966]</td>
</tr>
<tr>
<td>6</td>
<td>Kleinman-Langreth [1967, 1969a,b]</td>
</tr>
<tr>
<td>7</td>
<td>Shaw-Pynn (1969)</td>
</tr>
<tr>
<td>8</td>
<td>Singwi-Sjolander-Tosi-Land [1970]</td>
</tr>
<tr>
<td>9</td>
<td>Toigo-Woodruff [1970]</td>
</tr>
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<td>10</td>
<td>King-Cutler [1971]</td>
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<td>11</td>
<td>Mahanti-Das [1971]</td>
</tr>
<tr>
<td>12</td>
<td>Overhauser [1971]</td>
</tr>
<tr>
<td>13</td>
<td>Vashistha-Singwi [1972]</td>
</tr>
<tr>
<td>14</td>
<td>Srivastava [1977]</td>
</tr>
<tr>
<td>15</td>
<td>Taylor [1978]</td>
</tr>
<tr>
<td>16</td>
<td>Ichimaru-Utsumi [1980a,b, 1981a,b,c]</td>
</tr>
<tr>
<td>17</td>
<td>Sarkar et al. [1998]</td>
</tr>
</tbody>
</table>

The conduction electron density in $d(f)$ band materials is non-uniform due to quasilocalized character of $d(f)$-electrons. The density response function method is well suited to study the response of non-uniform electron density to the ionic motions. However, two questions are to be resolved:
How to account for the electronic band structure in the calculations of 
\( \epsilon (\mathbf{Q} + \mathbf{Q'}, \mathbf{Q} + \mathbf{Q'}) \) and then how to invert this infinite dimensional dielectric matrix.

As has been done with almost all the calculations of physical properties of 
\( d \)-band metals with local model pseudopotential, in the present study also, we shall use simple approach to dielectric function and hence we do not discuss the above mentioned questions and limit ourselves with the mention of some important references [Ferreira (1971), Ferreira and Parada (1971), Ferreira and Pratt (1971), Hanke and Bilz (1972), Hanke (1973), Sinha, Gupta and Price (1971, 1974), Hanke and Bilz (1971), Prakash and Joshi (1970, 1971), Singh and Prakash (1977)].

In the following, we summarize the work on the applications of local model potentials to study the physical properties of completely filled and empty \( d \)-band metals. We have not included here the partly filled \( d \)-band metals, in detail.

2.2 A Brief Historical Survey of Various Applications of Local Model Potentials to completely filled and Empty \( d \)-band Metals

Nand et al. [1976a,b] have used the model pot (Eq. (2.38)) to calculate phonon dispersion, binding energy and compressibility of \( Ag \) and \( Au \). The core overlap interaction was taken on the lines of Moriarty [1972a,b,c]. These authors used Singwi’s et al. [1968] local field correction in dielectric function. The results are reasonably good except for transverse phonons.
Kulshrestha et al. [1976a,b] used Eq. (2.54) to calculate phonon dispersion and elastic constants of noble metals. A reasonably good agreement between the computed and experimental dispersion curves and elastic constant was found except the shear elastic constant $C_{44}$.

Upadhyaya and Sharma [1977] have used Eq. (2.55) which is a one parameter local model potential to calculate liquid metal resistivity and binding energy of gold in connection with a dielectric function in the non-interacting band scheme. The results are found to be satisfactory.

Electrical resistivity of noble and transition metals were calculated by Khanna and Jain [1981b] using Animalu's model potential with reasonably good agreement with the experiment.

Nand and Tripathi [1977] calculated the phonon dispersion curves of Cu and Ag on the basis of their own pseudopotential.

Upadhyay and Dagens [1979] have calculated phonon frequencies in three symmetry direction using resonant model potential in its full non-local form. A very good agreement is found between the calculated and experimental results.

Starkloff and Joannopoulos [1977] have generated local pseudopotential for both valence and outermost core-shell. These authors calculated the density of electronic states. They also calculated the $4p$ core absorption spectra.

Kumar and Hemkar [1978] calculated the phonon dispersion curves of Au,
using the model potential given in Eq. (2.40).

Kulshrestha and Upadhyaya [1976a,b; 1977] computed the phonon frequencies of noble metals using transition metal model potential of Animalu [1973]. They used the dielectric function in the non-interacting band scheme.

Model potential given by Eq. (2.55) was used by Sharma [1978] to study the electronic properties of noble metals. This author, in this study, computed the phonon frequency, binding energy and liquid metal resistivity.

Barua and Singh [1978] determined the model potential parameters of Harrison's local modified point ion model with second order elastic constants of Gold. They compared their form factor with that obtained from Fermi surface data and calculated the third order elastic constants.

Kumar and Upadhyaya [1978] have assessed the non-local effects in the lattice dynamics of noble metals using TMMP of Animalu [1973].

Yamada [1978] calculated the band structure of Cu using the model potential of eqs. (2.47) and (2.48). The results obtained agree well with other methods.

George et al. [1978] used the potential (Eq. (2.39)) to calculate the phonon dispersion in noble metals. The conduction electron screening was treated on the lines of Vashistha and Singhwi [1972] and the overlap potential according to Moriarty. The potential parameters were fixed by fitting with zone boundary frequencies.
Khanna [1979] has used a local model potential to calculate second order elastic constants of Cu and Ag. He used the homogeneous deformation method and got good agreement between calculated and experimental values, except $C_{12}$ of Ag.

Sarkar and Das [1979] have calculated phonon dispersion in Au using a model developed by them to account for three body forces in phenomenological way.

Upadhyaya [1979] carried out the calculations of phonon dispersion in noble metals using resonant model potential of the form

$$v_o(E) = \omega_o(E) + v_{res}(E)$$

where $\omega_o(E)$ is the standard HA type model potential and $v_{res}(E)$ the resonant non-local potential acting on $d$-states. He found that local form of HA type for $\omega_o(E)$ generated good results.

Vrati et al. [1979] used Eq. (2.44) to calculated phonon dispersion in Ag. They found that the results of transverse branches heavily depend on core-overlap contribution.

Kumar and Upadhyaya [1979] has constructed the energy wave number characteristics by considering $E$ and $k - q$ dependent linear terms in the form factor expansion and used the TMMP of Animalu in resonance form to calculate phonon dispersion in noble metals. The dispersion curves are reasonably raised relative to the local approximation results.
Vrati et al. [1980] have been able to explain phonon anomalies in Ni, Pa and Pt with the help of one parameter model potential.

Singh et al. [1981a,b] have used a local pseudopotential to account for phonon spectra of Ta. The same model was used for Nd also [Singh (1981a,b; 1982)].

Upadhyaya [1981] has examined the effects of Van der Waals forces on the lattice dynamics and crystal structure of noble metals. The resonant model + van der Waals forces lowered the results by 5-8%.

Khanna [1981b] used Eq. (2.49) to compute form factors, inter-atomic potential, liquid metal resistivity, thermoelectric power and binding energy of Ag and Au. He also reported dispersion curves of Au.

Using the total crystal energy expression with the overlap potential energy by Moriarty and with the model pseudopotential by Kulshreshta et al., the pressure volume relations of noble metals were studied by Soma et al. [1981]. These authors also studied the elastic stiffness constants $B$, $C_{44}$ and $C'$ under pressure using homogeneous deformation method.

Oli [1982] has discussed the importance of local field correction in the lattice dynamics of Nb.

Idrees et al. [1981] presented an analysis of the model potentials proposed for Copper, Silver and Gold. Three tests based on the calculation of band gaps, liquid metal resistivities and thermo-electric power were carried out. The numerical results obtained were compared with the corresponding experimental values. A comparative study of model potentials due to Borchi
and De Gennaro [1970], Animalu [1973], Kulshrestha et al. [1975] and Sharma [1978] was carried out. It was concluded that the pseudopotential of Borchi and De Gennaro is the only one giving some overall agreement with experiment. It is pointed out that $s - d$ hybridization contribution in the Borchi - De Gennaro pseudopotential needs to be suitably modified if closer agreement with the experiment is to be achieved.

Upadhyaya and Dagens [1982] has investigated relativistic effects on the lattice dynamics of gold. He carried out such a study in the context of resonance model potential.

Kumar and Sharma [1982] used Eq. (2.55) to study dispersion curves, binding energy, compressibility and elastic constants of Cu.

Lin Guang and Li Shu [1983] have extended the pseudopotential application to calculate Hugonist curves of noble metals. Finnis and Sinclair [1984] have given real space analysis of interatomic forces to explain phonon anomalies in b.c.c. 3$d$ transition metals. This analysis is equivalent to Verma-Weber's theory.

Alam-Tomak [1984] have calculated the dependence of electrical resistivity in liquid Ag – Au; Cu – Ag; Cu – Au binary alloys on composition. They used the model potential proposed by Idress et al. [1982] (Eq. (2.56)).

In the above given discussion we have mainly given the historical survey up to 1984 for noble metals. The empty $d$-band metals, Ca, Sr and Ba which are diivalent will be considered now.
The experimental results on the phonon spectra of alkaline earth metals (empty d-band metals) started coming from 1983 [see, for example, Stassis et al. (1983)]. Hence, the theoretical work on lattice mechanical properties of these metals was scanty up to 1983.

Animalu [1967] used a local approximation of the Heine Aberankov model potential and calculated $\omega(q)$ for Ca, Sr, Ba. The transitions induced by temperature and pressure between the f.c.c. and b.c.c. phase were analysed by computing the differences in Gibbs free energy between the two phases in harmonic approximation.

Dagens [1976, 1977] applied his resonant model potential (RMP) to Ca and calculated the pseudopotential form factor, the total energy and elastic moduli. Sanno et al. [1976] have calculated the pressure derivatives of pseudopotential form factor at $0^\circ K$ and $293^\circ K$; the results were poor.

Upadhyaya and Animalu [1977] applied their rare earth model potential (REMMP) which is an extension of the transition metal model pseudopotential [Animalu (1973)] to rare earth metals but no study was made by them on the alkaline earth metals.

Gurskii and Krasko [1971] used their own model potential with an ionization energy as an input parameter and with HSGV screening for Ca, Sr and Ba. Taut and Eschring [1976] used the Show non-local energy dependent optimized potential with the VS screening in a calculation of $\omega(q)$ and $f(\omega)$ and band structure of Ca. Similar work has also been reported by Ker [1976] for Ca, Sr and Ba, who calculated the phonon spectra for all these three metals along with band structure of f.c.c. Ca. The results obtained by
Taut and Eschring are in reasonable agreement with the thermodynamic Debye temperature $\theta_D$ but rather different from the results of Animalu. The $d$-bands of the alkaline earth metals lie not very far above the Fermi level. However, Taut and Eschring relied on an argument by Moriarty [1972] that $s-d$ hybridization has little effect on the vibrational properties in this case and can be neglected. Appapilai and Williams [1973a,b] have also treated these metals as simple metals and have calculated electrical resistivity of $Ca$, $Ba$, $Sr$. These results were found to be poor.

Rasolt and Taylor [1975] have given a scheme to account for non-linear effects in the screening by conduction electron. The scheme includes the consideration of induced charge density due to implantation of ion in electron gas. Based on this scheme these authors have constructed the interatomic potential for $Ca$.

Moriarty [1983] calculated the phonon spectra of $Ca$ and $Sr$ from a first principle generalized pseudopotential theory which accounts for full effects of $d$-band hybridization. The results obtained agree with the experimental data to within 10%. On the other hand, there exist several calculations [Sharma and Kachhava (1981), Moriarty (1972a,b,c, 1973, 1977, 1982, 1983)] on the phonon dispersion curves of b.c.c. $Ba$. All these calculations were performed within the framework of the pseudopotential theory of metals. The phonon frequencies calculated by Animalu [1967] and Sharma [1981] using local pseudopotentials are substantially higher from the measured values. Furthermore, in both these studies [Animalu (1967), Sharma (1981)], the phonon frequencies of $L(q,0,0)$ branch were higher than those of the $T(q,0,0)$. Moriarty [1972, 1973, 1977, 1982, 1983] calculated the zone boundary frequencies along some high-symmetry directions using a generalized pseudopotential approach which incorporates

50
the effects of hybridization of free electron states with $d$-states. The results obtained, however, are better than those obtained by Animalu [1967] and Sharma [1981], but are higher than the experimental values and fail to reproduce the observed peculiarity.

Sharma and Kachhawa [1981] have also used a local pseudopotential for Ca. From band structure calculation Vasavari et al. [1967], Johansen [1969], Johansen and Mackintosh [1970], Jan and Skriver [1981] and Madan [1998] it has been observed that below the Fermi level, the electronic band structure of these metals lies in close proximity to the Fermi level. However, the electronic wave function at the Fermi level contains an admixture of $d$-band character.

Prasad et al. [1984] have used their Krasko-Gurskii model potential to compute lattice dynamics of f.c.c. calcium. The anomalous dispersion and anisotropies have been explained by the model potential approach.

Gupta [1984] has proposed a one parameter model to calculate phonon spectra and Debye temperature of noble metals. This model satisfies the Cauchy relation and the symmetry requirements of the lattice and also the equilibrium condition. Phonon frequencies and Debye temperatures calculated for Cu showed good agreement with experiments.

Jankowski and Tsakalokos [1985] have explained the enhancement of elastic moduli due to stress using second order perturbation in pseudopotential. The theoretical expression $C_{44} = \frac{1}{3} (2C_{11} - C_{12})$ is in better agreement with the experiment than the Cauchy relation $C_{44} = C_{12}$ for f.c.c.
noble metal crystals [see also Milstein and Rasky (1985)] in which pseudo-potential calculations of elastic constants of Cu and Ag are given].

Phonon dispersion relations for noble metals were studied by Gohel et al. [1985] on the basis of the pseudopotential due to George et al. [1978]. The cardinal interest was to study the relative importance of axially symmetric and general tensor forces between the nearest neighbours and to explore the possibility of a simple pseudopotential for noble metals. It was found that the tensor forces up to first neighbours do play an important role and that a simple pseudopotential can be used as a working potential to study the phonon dispersion curves of noble metals.

Yurev and Vatolin [1984] have proposed a model potential including resonant and non-resonant contributions. It permits the satisfactory description of atomic and electronic properties of transition metals.

A non-local model pseudopotential was used by Pilyankevich and Zakaryan [1986] to calculate physical characteristics of transition metals. The pseudopotential is presented as a sum of two terms the first of which structurally coincides with a pseudopotential of simple metals. The second one takes into account a $s-d$ hybridization and resonance and is approximated by a function depending on the Fermi energy of electrons in crystals. The authors have calculated the binding energy and lattice parameter.

Gupta et al. [1986] have used the model potential due to Nand et al. [1975, 1976b] to compute phonon spectra of Ba. In this case, the calculated frequencies of the transverse branches were found to be higher than those of the longitudinal ones in the [100] direction when the local field correction
in the Hartree dielectric function was taken into account on the lines of Singwi et al. [1968]. This anomalous feature of the dispersion curve in $Ba$ was attributed to the hybridization between free electron states and $d$-states.

Mohammed et al. [1984] used a model of Morse potential immersed in electron sea to calculate phonon dispersion, debye temperature, mean square displacement, effective X-ray characteristic temperature and Debye-Waller factor exponent as function of temperature. The results are in excellent agreement with experimental data. These authors describe a metallic atom as being composed of ionic interactions described by Morse potential with the ionic lattice immersed into a sea of free electron gas. The electron interaction is described by means of a screened Coulomb interaction. Note that this method does not involve electron ion interaction model potential but it models the interionic interaction. The metals studied are $Cu$, $Ag$, $Au$, $Pb$, $Pa$ and $Ni$.

Thakur [1986] has calculated $\theta_D$ for different temperatures on the basis of electron ion interaction which is taken as screened Coulomb type. The ion-ion interaction was evaluated applying the valence force field.

Soma et al. [1987] have studied the pressure effect on the melting temperature of copper by use of Lindemann's melting law. The phonon frequencies necessary for such calculation were generated from the model pseudopotential due to Kulshreshtha et al. [1975].

Onwuagba [1984] has applied his scheme considering local field effects through screening of Born-Mayer type potential to $V$, $Nb$, $Ta$. 
One parameter model potential (Eq. (2.56)) was used by Khwaja and Razmi [1986] to calculate binding energies and elastic constants of Cu, Ag and Au. The results were compared with experimental data and other calculations.

Gupta et al. [1987] extended their above mentioned study to b.c.c Sr. In this case, they obtained reasonable agreement with experiment, especially, the restoration of the order of longitudinal and transverse branches in [100] direction with local field correction of Sham and Ziman [1965].

The question whether one can give a consistent description of the phonons in b.c.c. and f.c.c. Ca cannot be answered by a comparison of the Born-von Karman parameters. The simplest scheme which allows the calculations of the phonons with the same parameters for both structures is a local pseudopotential [Heine and Weaire (1970), Animalu (1967)]. Though the applicability of this scheme to Ca is doubtful because of the proximity of d band to Fermi surface [Jan and Skriver (1981)]. To study the problem mentioned just above Heiroth et al. [1986] have employed a model pseudopotential adequate for simple s–p metals [Krakso and Gurskii (1969)]. Though a fit with the same pseudopotential in both phases could reproduce the general features of the phonon dispersion, there are considerable deviations in some phonon branches especially at low frequencies. In the f.c.c. phase there is even a violation of the stability condition. Since this result was obtained for different pseudopotentials [Aschroft (1966), Nand et al. (1976b)], it was concluded that the local pseudopotential picture is too simple for Ca. The local field correction used by these authors was that due to Ichimaru and Utsumi [1981].
Upadhyaya and Kulshrestha [1987] have also studied the phonon spectra of f.c.c. Ca using a model potential.

Wang and Overhauser [1987a,b] have modelled the pseudo-ion charge-density in the spirit of pseudopotential theory and obtained good agreement with experimental phonon dispersion curves of twelve metals including Cu, Ag and Au.

Zhovtanetskii et al. [1984], using completely orthogonalized plane waves, have given general structure of model potential containing $s-d$ interaction.

Upadhyaya and Kulshrestha [1987] have used the resonant model potential to compute dispersion relation in Ca. The results are in good agreement with experiments.

Soma et al. [1987] have calculated the temperature dependence of the mean square displacement of noble metals using the treatment of lattice dynamics on the basis of model potential of Kulshrestha et al. [1975, 1976]. The Debye temperature at higher and lower temperatures was also estimated using Debye's model. Then using the volume dependence of mean square displacement the pressure effect on the melting point of Ag and Au was studied by Lindemann's melting law. The melting curve was found to increase as function of the compressed volume.

Neutron scattering experiments on single crystals of b.c.c. Ba have revealed that the longitudinal branch along [100] direction is lower than the transverse branch. This anomalous behaviour has been studied by Chen et al. [1986], with the use of the frozen phonon method.
Onwuagba and Pal [1987] have used a screened Born-Mayer potential along with transition metal model potential to study lattice dynamics of Nb and Ta.

Katsnelson et al. [1987] have used Animalu's model potential for transition metals to calculate the total energy and equilibrium atomic volumes of compact (f.c.c., b.c.c. and h.c.p.) modifications of 24 transition metals. The calculations indicate that there are elements that can be described both more and less satisfactorily by this potential.

Prakash and Upadhyaya [1988] have considered the interaction system composed of two body and many body parts. These authors use a short range three body potential to account for the many body forces. The model potential of Animalu was used with these additional forces to compute the phonon dispersions in Cu, Ag and Au.

Kafif and Gasser [1988] have studied the temperature variation of resistivity of Ag using a form factor deduced from the model potential which takes into account the d-band like the Moriarty potential [1972].

A comprehensive unified study on f.c.c. alkaline earth metals, Ca, Sr and the b.c.c. phase of Sr and Ba was made by Das and Sarkar [1987]. The properties studied were equilibrium lattice parameter, total energy SOE constant, pressure derivatives of SOE constant and phonon spectrum in symmetry directions. The results obtained showed an overall agreement with the experiment. The results partially reproduce experimentally observed phonon cross-over in Ba. This was attributed to many body effects.
Singh et al. [1988] have written two body interaction as the sum of $s - s$, $d - d$ and $s - d$ contributions. The free electron part of the pair potential is obtained in second order perturbation theory using a rational dielectric function and the empty core pseudopotential. The overlap between $d$-states on different ions and the effect of $s - d$ hybridization are included in an approximate manner, as has been suggested by Wills and Harrison [1983]. An approximate temperature dependence has been included in the effective potential through an asymptotic factor. These potentials have been used to calculate phonon spectra of $Cu, Ag, Au, Ni, Pd, Pt$ and $Fe$ in real space. The binding energies and elastic constants are also calculated.


The pressure induced b.c.c.-h.c.p. phase transition in $Ba$ has been studied by Chen et al. [1988] using first principle total energy calculations.

Vaks et al. [1988] have found that in b.c.c. alkaline earth metals the short wave phonon frequencies of the soft $\Sigma_4$ branch increase with temperature and mode Gruneisen parameters sharply decrease. These effects are in increasing order in the $Ba-Ca-Sr$ series.

Onwuagba [1981] observed that in the context of model potential, the off diagonal components of the interatomic potentials $\phi_{(sd)-f}$ and $\phi_{f-(ds)}$ associated with $s - d$ and $d - s$ interactions in the $s$ and $d$ electrons make
significant contribution via the local fields in the phonon spectrum of f.c.c. Lathanum.

Oli [1988] has developed a method of deducing a transition metal ion potential from a knowledge of the phase shift $\eta(k)$. The method used is based on the distorted plane wave scattering approximation for the deduction of non-singular potentials from scattering phase shifts in an inverse-scattering approach. The resulting electron ion potential obtained is a finite Dirichlet series sum of short range exponential functions. The Fourier transform of the potential is obtained for applications in the area of transition metal solid state physics.

A semi-empirical model to simulate thermodynamic properties of f.c.c. transition metals has been proposed by Rosato et al. [1989]. In this method, the attractive energy is derived within a second moment approximation of the tight binding scheme. The repulsive pairwise interaction is assumed to be of Born-Mayer type and the parameters of the potential have been adjusted on the bulk modulus, the elastic constants and the cohesive energy. These authors, along with other properties, calculated the root mean square displacements and thermal expansion of Cu and Ni.

Chopra and Laziz [1988] have argued that microscopic theories indicate the existence of 3-body forces in noble metal. To account for these 3-body forces, these authors have proposed a phenomenological model. The phonon dispersion curves of Ag calculated on the basis of this phenomenological model show good agreement with experiments.

Lee et al. [1988] have calculated the elastic constants of Cu using a volume
parameter potential function derived from the cohesive energy with an assumption that cohesive energy can be written as a sum of pair interaction energies. This potential is relatively weak bonding and long ranged as compared with the Johnson-Wilson experimental pair potential function. Mishra and Singh [1988] have given a simple model for lattice dynamics of transition metals. In this model ion-ion interaction is evaluated by applying the valence force field. The electron-ion interaction is simple screened Coulomb type.

Takeuchi et al. [1989] calculated the equilibrium ground state properties of \( Ag \) and \( Au \) using first principle norm conserving pseudopotentials. These authors have obtained the cohesive energies, bulk modulli and lattice constants that are in very good agreement with experiments.

Aradhana and Rathore [1989] have modified the Morse potential to represent the three body forces among the common nearest neighbours of b.c.c. \( Ca \) and \( Sr \). The importance of three body forces is made clear and loud as these forces impart the proper slope to the dispersion curves and lead to an adequate Cauchy's discrepancy in various orders of elastic constants.

Using the form factors of Animalu and Moriarty [1973], Akinlade and Hussain [1988] calculated the temperature dependence of electrical resistivity of noble metals at constant volume and pressure.

Wang and Overhauser [1988] have generalized the pseudopotential model of the phonon spectrum of a liquid or amorphous metal.
Chelikowsky and Chou [1988] have examined the electronic and structural properties of elemental copper using pseudopotentials and a local orbital basis consisting of Gaussians. They found that one can use a much weaker ionic pseudopotential to describe accurately the measured band structure, cohesive energy, lattice constant and compressibility. They also find that the energy versus volume curve for copper in b.c.c. structure does not exhibit a double minimum.

Silonov et al. [1988] have calculated the electrical resistivity of Cu, Ag and Au liquid metals by using Degen's pseudopotential in an approximation of linear screening. The results agree satisfactorily with experimental data.

Gann and Pekhedyasheij [1988] have developed the pseudopotential theory for metals. In this work, unitary transformation of the plane wave basis to a completely orthogonalized plane wave basis is obtained. This permits the derivation of an expression for the Hermitian pseudopotential of single metals.

A theory for calculating vibrational spectra of transition metals has also been given by Kushwaha et al. [1989]. This is a semi-first principle model. The theory uses the concept of a rigid shell moving relative to its nucleus to simulate the response of the $d$-electrons. The long range interaction between ion-ion as well as shell-shell via conduction electrons is described using the screened potential and a short range interaction is described using two and three body forces between cores and shells. This model was applied to Zr, Hf and Ti.

Onwuagba [1989] extended the application of his previous result that local
field correction can be accounted for with the help of an attractive Bcrn-Mayer type term, to molybdenum and tungsten. It was shown that with an appropriate model potential the soft modes in both metals could be understood.

A fast converging temperature dependent pair potential has been proposed by Singh et al. [1988]. This method was extended by these authors to b.c.c. transition metals [1989].

A simple model for the bond energy in the framework of pseudopotential theory has been proposed by Antonov et al. [1988]. The applicability of the model has been demonstrated taking into account the interaction of d-electrons, the definition of elastic models, the equation of state and the sound spectrum of Pt in a wide pressure range.

The Embedded Atom Model (EAM) has been applied to calculate the phonon frequencies of transition metals Ni, Pd and Cu by Ningsheng et al. [1939]. It was found that EAM with the first neighbour potential cannot assure to reproduce the phonon frequencies at zone boundary.

Onwuagba’s scheme of incorporating local field correction to the dynamical matrix was extended to molybdenum and tungsten by Okoye and Pal [1990].

Cohesive energies, bulk moduli and equilibrium lattice constants were calculated for 4d and 5d metals by Elsasser et al. [1990]. These authors have used an ab initio pseudopotential.
Antonov et al. [1990a,b] have used a simple pseudopotential model for the calculation of the phonon spectra at the equilibrium volume and under pressure. The model is based on the second order perturbation theory with the local model potential acting on the $s$-electrons while the $d$-electrons contribution is simulated by the repulsive Born-Mayer interatomic potential. Pressure influence on the lattice properties was studied for small compressions (mode Gruneisen parameters) as well as for ultra high pressure (equation of state up to 1 TPa). The results of lattice dynamics calculations were used for determining temperature dependence of the lattice heat capacities and of the macroscopic Gruneisen parameters. The model parameters were determined for ten f.c.c. transition metals $Cu$, $Ni$, $Fe$, $Co$, $Ag$, $Pd$, $Rh$, $Au$, $Pt$ and $Ir$. This model was used for the calculation of the phonon dispersion and the density of states as well as for the elastic constants and their pressure derivatives. Good agreement with experimental data was obtained.

The pair potential defined for transition metals previously [Singh et al. (1988)] was extended to study the phonon dispersion of alkaline earth metals [Singh and Singh (1990a,b)]. The temperature dependence was included through an asymptotic factor. The dispersion curves agree with experiments to within 10%, except for few wave vectors at zone boundary. The binding energies and elastic constants were also calculated.

Singh [1990a,b] has written the effective pair potential for $d$ and $f$ shell metal as the sum of $s-s$, $d-d$, $s-d$, $f-f$ and $s-f$ contributions and carried out the calculations of phonon dispersion curves of $Tb$ and $Ho$.

Singh [1990a,b] has studied the mechanical stability of $Cu$ under the linear distortion in [100] direction, using a simple pseudopotential.
A plane wave basis has great advantage for many calculations in the physics of solids. To apply this basis to a wider class of materials, the atomic characteristic of a pseudopotential is identified which leads to rapid convergence in the solid and a new method for generating pseudopotential optimized according to this criterion was given by Rappe et al. [1990]. These authors carried out the calculations of structural properties of f.c.c. copper using \textit{ab initio} plane wave basis.

Mo Li and Goddard [1989] have suggested interstitial electron model for lattice dynamics of f.c.c. metals including noble metals. This model treats the valence electrons as classical lattice particles localized at interstitial tetrahedral positions.

Vaks et al. [1989] have suggested the use of interionic potentials obtained in the second order relative to the electron-ion interaction pseudopotential $V_{\text{ion}}$ to the modelling of lattice defects in transition metals. Appropriate adjustable $v_{\text{ion}}$'s are proposed.

Yokayama et al. [1989] have suggested a method of extracting anharmonic interatomic potential from extended X-ray absorption fine structure.

Straub et al. [1988] have studied the elastic moduli of Cu under compression at 0\(^\circ\)K up to 1 Mbar. These authors have used a simple empty core model for $s$-electrons. The $d$-electron interaction was considered in tight binding theory.
Mishra et al. [1991] have also modified the Morse potential to include 3-body forces in transition metals. The potential so constructed was used to calculate phonon dispersion curves for Pb, Pd and Pt.

In a very important extension of his theory for filled and unfilled d-band metal theory based on density functional formalism, Moriarty [1988] has obtained useful expressions, in real space, for energy and multi-ion interactions.

Silonov et al. [1990] have obtained the expressions for form factor of a model Hamiltonian and characteristic functions within the framework of the resonant model potential.

Mishra [1990] has developed a three body force model on the basis of Morse potential.

Dynamical model, discussed previously, involving s–s, d–d (overlap), c–d attractive, f–f (overlap), f–f attractive interactions, rational dielectric function and H–A model potential was applied to calculate, binding energy, phonon dispersion and elastic constants of some f-shell metals by Singh and Singh [1990].

Moriarty [1990] has given an analytical expression for multi-ion interaction in transition metals. This work is based on his first principle density functional approach.

Bylander and Keinman [1992] have introduced a new projection operator replacing old one in Phillips-Kelinman pseudopotential approach. The
pseudopotential so constructed is applicable to cases such as 3d and 2p valence functions that have no core functions of the same symmetry.

Singh et al. [1993] have developed a force constant model which accounts for two and three body forces and calculated the dispersion curves and elastic constants of Co and Te metals.

Mishra et al. [1992] have modified the generalized Morse potential to study lattice dynamical properties of f.c.c. metals.

Singh et al. [1992] have applied generalized exponential potential along with Born-Mayer potential to study lattice dynamics of Sc, Zr and Mg.

Barrera and Batana [1993b] have obtained general expressions to calculate the first, second and third order coupling parameters considering a general interionic model that includes both two and three body uncoupled forces. These formulae are applied to deduce the analytical expressions of the pressure and second and third order elastic constants and the dynamical matrix and its strain derivative for the case of metals with f.c.c. structure. The two body forces are considered upto third neighbours while 3-body forces upto nearest neighbours are taken. The model uses four independent parameters. The metals studied are Ni, Pd and Pt.

Onwuagba [1993] has obtained the screening of short range Born-Mayer potential for alkaline earth metals in the framework of the resonance pseudopotential model. The elastic constants were calculated in the long wavelength limit of phonon dispersion. The numerical calculations show that the attractive component of the potential explains the soft modes in the
b.c.c. barium.

The transport properties of liquid transition metals are discussed by Ononiwu [1993] on the basis of Ziman's theory, as generalized by Evans, Greenwood and Lloyd. The effect of d-band resonance in transition metals is simulated in the nearly free electron approximation where the ordinary (V-matrix) pseudopotential form factor is replaced by the T-matrix form factor in the transport integral. The T-matrix form factor is derived in a closed form the transition metal model potential V-matrix form factor by solving the appropriate T-matrix integral equation.

Yokoyama et al. [1993] have shown that the simple metal theory may describe the structure of liquid rare earth metals when the pseudopotential parameters are properly selected. This point has been tested for liquid La, Ce, Pr and Nd. The core radius of Aschroft's empty core model was uniquely determined by the density of liquid and the effective valence $Z_{\text{eff}}$ was estimated from the value of the plasma parameter.

Inspired by the ab initio generalized valence-bond calculations of small metal clusters, Mo Li and Goddard [1993] proposed a phenomenological many body interaction model, the interstitial electron model (IEM) for interaction of ions and electrons in metals. Simple pair potentials are used for ions and interstitial potentials. This model was applied to study lattice dynamics of Cu, Ni, Ag, Au, Pd, Pt, Al, Ca, Ba and $\gamma$-Fe.

To study thermal expansion of f.c.c. metals Barrera and Batana [1993b] have proposed an interionic potential that considers both two and three
body uncoupled forces that allows for the separate evaluation of both contributions. Here the aim was to develop a simple model that can explain a broad spectrum of lattice properties.

The phonon dispersion curves of $\gamma$–Fe have been computed in the framework of the transition metal model potential including the short range 3-body interactions.

Original local model potential due to Sharma and that modified by Idrees et al. were used to calculate lattice dynamics of $\alpha$–Fe by Boselli and Gupta [1993]. The results were not very satisfactory. The reason for this is that the potentials considered are not continuous at $R_M$ and $R_W$ in real space.

There are presently experimental data on f.c.c. metals concerning both fundamentally harmonic and anharmonic properties. At present there is not a simple interionic potential that can adequately reproduce all these experimental information. Barerra and Batana [1992] have developed several programmes to calculate the general central two-body interaction up to 19th neighbours and nearest-neighbour 3-body interactions.

Sugiyama [1992] has developed an asymptotic form of two body interionic potential in metal at non-zero temperature.

Singh and Yadav [1994] have used previously mentioned real space analysis to calculate binding energy and elastic constants of f.c.c. transition metals.
Shukla [1994] has evaluated quasi-harmonic and anharmonic contribution to atomic mean square displacement or Debye Waller factor of f.c.c. metals. The interionic potential used in this work is the Lennard-Jones potential.

Moriarty [1994a,b] has carried out the calculations of first principles pressure temperature phase diagrams for simple and transition metals. The metals, he studied, are Mo and Fe.

Sugiyama [1994] has extended his work on asymptotic expression for the interionic potential at non-zero temperature.

Using multi-ion interionic potentials derived from first principles generalized pseudopotential theory together with the molecular dynamics, a detailed study of melting and related high temperature and related solid and liquid properties in Mo has been performed by Moriarty [1994a,b].

Upadhyaya et al. [1994] have used angular forces of Clerk, Gazis and Wallis type to calculate phonon dispersion in Be, Tb, Ho and Lu.

Mishra et al. [1993] have given a modified scheme centred around Morse potential to account for 3-body forces in the lattice dynamics of f.c.c. metals. This exponential potential is less parametric and incorporates exchange and correlation effects due to electrons in a simple and effective manner. The model has been applied to study dispersion curves, elastic constants and zero point energy.

Guong [1994] has obtained a force constant tensor for Au, using the plane
wave based linear response method. The phonon dispersion curves so obtained are in excellent agreement with experiment.

Okoye and Pal [1993] have studied the phonon dispersion in noble metals by incorporating a short range 3-body interaction, a Born-Mayer repulsion with Animalu's model potential.

Quong et al. [1993] have given a method for the self-consistent determination of interatomic force constants using non-local \textit{ab initio} pseudopotentials.

Saxena et al. [1995] have employed Aschroft's empty core model to construct the temperature dependent interionic potential for rarely studied b.c.c. Ti, Zr and Hf.

Osman and Mujibur Rehman [1995] have calculated structural and thermodynamical properties of 3d transition metals on the basis of pseudopotential theory. In this theory $s-p$ and $d$ electrons are treated separately. The $s-p$ electrons are treated in terms of the conventional second order pseudopotential theory, while the lightly bound $d$-electrons are treated in terms of the Wills-Harrison prescription that makes use of the Friedel rectangular electron density of states. The prediction of the structural phase stability and other relevant thermodynamic properties are found to be consistent with experiments.

Okjun [1995] has used a $N$-body potential energy function, constructed empirically to study the dynamical behaviour of Cu and Ni. This potential
energy function contains both two and three body interactions. The parameters of the potential are determined by a method similar to that given by Girifalco and Weiser [1958]. The input data are independent of phonon frequencies. The calculated phonon dispersion curves in major symmetry directions are in good agreement with experiments.

Datta et al. [1995] have shown that pseudopotential third order energy plays an important role in explaining lattice mechanical properties of HCP metals, however, it gives unphysical elastic properties. The root of this unphysical contribution may be identified with the singularity in the derivative of the \(g\)-function appearing in the expression for the third order energy. They have resolved this problem by imposing a consistency condition in second order theory.

Isoardi et al. [1995] have proposed a simple model of interionic interaction that includes two and three body forces to compute wide spread of properties for a wide variety of metals. The properties considered are: (i) dispersion curves, (ii) mode Gruneisen parameters, (iii) specific heat, (iv) Gruneisen function, and (v) second and third order elastic constants. The model was applied to potassium.

De Girocoli [1995] has successfully computed phonon dispersion curves of \(Nb\) using density functional perturbation theory.

Lattice dynamical calculations have been performed in real space approach using Rare Earth Metal Model potential for H:CP rare earth metals by Singh [1995].
The generalized form of exponential potential was extended by Verma et al. [1996] to account for: (a) a realistic realization of interactions in all separations, and (b) three body and electronic effects. This model is free from usual fitting procedure. This model was employed to compute the cohesive energy, phonon spectra and second and third order elastic constants of V and Nb. The computed results show good agreement with experiments.

Coelho and Shulka [1996] have modified the original model of Sarkar et al. to account for three body forces in noble metals. The reasonable agreement with experimental findings was obtained.

Pavone et al. [1996] have presented some applications of a first principle approach to the study of the vibrational properties of crystals. The ab initio lattice dynamics is studied by means of a perturbative approach to the density functional theory. The validity of this method is investigated by performing the calculations of the phonon frequencies of crystals with different structure and bonding properties. The results obtained are in excellent agreement with the available experimental data.

Raju et al. [1996] have calculated the electronic contribution to the Debye temperature of transition metals using the Wills-Harrison model.

Saxena et al. [1995a,b] have computed phonon frequencies and elastic constants of some scarcely studied transition metals i.e. b.c.c. Zirconium and b.c.c. Titanium, with a model pseudopotential involving core and ionic radii.

In the analysis presented by Akgun et al. [1997] the interaction system of
an f.c.c. d-band metal is considered to be composed of two body and three body parts. A new three body potential has been developed to consider its contribution to dynamical matrix. The metals studied are Ni, Pd, Cu and Ag. The parameters defining the two and three body potentials are evaluated from equilibrium pair energy, bulk modulus and total cohesive energy.

The work by Barrera and Tendler [1997] describes the implementation of a new program EAMLD that allows the calculation of static and vibrational contributions to the free energy of metals and alloys using lattice dynamics in quasi-harmonic approximation. Many body interactions are taken into account by using potentials of the Embedded Atom Method form. The examples include the temperature dependence of elastic constants of Au.

Katsnelson et al. [1997] have proposed a simple pseudopotential model which allows the phonon spectra and temperature dependence of lattice heat capacity of Ir and Rh.

The universal form of embedding function suggested by Banerjee and Smith together with a pair potential of the Morse form have been used by Pohlong and Ram [1998] to obtain embedded atom method (EAM) potentials for f.c.c. metals: Cu, Ag, Au, Ni, Pd and Pt. The potential parameters were determined from elastic constants. The phonon spectra so obtained are in reasonable agreement with earlier calculations.

Very recently, Singh [1999] has studied structural phase transformation of Cu, Pd and Au using transition metal pair potential (TMPP), with temperature dependent damping factor [Takanaka
and Yamamoto (1977)]. Such effective potential was fitted to a Gaussian form and structural phase transitions of Cu, Pd and Au were studied down to volume $0.55 \Omega_o$, where $\Omega_o$ is observed atomic volume. All three metals are found to be most stable in f.c.c. phase at observed atomic volume. Cu and Au are found to transform f.c.c. $\rightarrow$ h.c.p. structure at volume (pressure) $0.78 \Omega_o$ (352.25 Kbar) and $0.70 \Omega_o$ (878.18 Kbar), respectively. The TMPP was also used to calculate cohesive energy, binding energy, bulk modulus and phonon spectra of these metals. Pollack et al. [1997] have recently used a density based local pseudopotential to compute lattice dynamics, elastic constants and liquid metal resistivity of 16 simple metals including Ca, Sr and Ba.

### 2.3 Conclusion

As stated at the outset of this chapter, we have given a brief survey of the work on alkaline earth metals. Some relevant references on partly filled $d$-bands are also mentioned. The following facts emerge from this survey:

1. Nearly more than half a dozen local model pseudopotentials have been constructed by considering different forms of potentials to represent phenomenologically the $s-d$ hybridization, in real space. Some people have used square well while some have used the triangular forms. Other analytical expressions have also been used. Although these authors consider Harrison's first principle pseudopotential formalism as the base, nobody attempted the form of $q$-space directly available from Harrison's theory.

2. Although there are large number of papers by different authors with different forms of model pseudopotentials, no attempt has been made to account for complete assessment of a single form in its ability to
predict at a time large number of physical properties of transition metals.

3. A series of papers by Moriarty on first principle approach are extremely important as they deal comprehensively with large number of physical properties. But this work is quite complicated and intricate and requires lengthy numerical calculations.

4. The work on empty $d$-band metals is scanty except the paper by Das and Sarkar (1987) who use a simple $H - A$ model potential and study about half a dozen properties of these metals.

5. The work by Antanov et al. (1990) is worth mentioning. These authors consider some transition metals including the noble metals. Again, these authors also use the simple $H - A$ model potential. No special form suitable for transition metals has been tried.

6. In many of the papers dealing with local model potential for $d$-band metals no due consideration has been given to core-core repulsion and local field correction due to $s - d$ hybridization.

The aim of the present thesis is to study the following points:

(a) Instead of going into phenomenology, in real space, to construct the model potential, we prefer the use of that form in $q$-space which is directly available from Harrison's first principle theory. This form is supposedly better than simple H-A model potential.

(b) We give a due consideration to local field correction due to $s - d$ hybridization on the line of Onwuagha by combining Born overlap repulsion with the type of the term suggested by him.

(c) To test the ability of our approach to predict various properties
we study at a time about 25 physical properties. In the determination of the parameters of the potential parameters we have used the most essential condition of equilibrium that is pressure $P = 0$ at $0^\circ K$.

(d) One of our aims is to see as to how far the results obtained in such a simple approach can be comparable to those obtained from Moriarty's first principle approach, and those obtained with other model potentials.

In the present thesis we consider alkaline earth metals.