CHAPTER 2

Construction of Model Potential for Transition Metals and Historical Survey
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2.1 First Principles Pseudopotentials for Transition Metals

Transition metals are characterized by $d$-bands. The $d$-bands in transition metals have finite width. These $d$-bands are neither free electron type nor like completely bound core states. This is due to the fact that $d$-states in transition metal get distorted by the crystal field. Thus $d$-bands states cannot be treated as either core states or conduction states. Thus, any theory of transition metals must give an appropriate treatment to $d$-states. It is in this regard that first principles transition metal pseudopotentials differ from those for simple metals. If one includes the $d$-states in conduction state then resulting pseudowave functions are not smooth and hence pseudopotential turns out to be strong. The strength of such pseudopotential rules out the use of perturbation method which is the main credit of pseudopotential theory. To overcome this difficulty, Harrison (1969) extended the pseudopotential theory based on orthogonalized plane wave...
method of calculating band structure, to transition metals. Harrison expanded the conduction band state $\psi_k$ in an over complete set which consists of conduction-band states, $|\vec{k}>$, core states $|\alpha>$ and atomic $d$-states $|d>$. 

$$\psi_k = \sum_n B_n |\vec{k} + \vec{g}_n > + \sum_\alpha A_\alpha |\alpha > + \sum_d C_d |d >$$  \hspace{1cm} (2.1) 

Here, $B_n$, $A_\alpha$ and $C_d$ are expansion coefficients and $\vec{g}_n$ are the reciprocal lattice vector. In fact, in the above expansion $|d>$ states should be quasi-localized crystal states. However, we may model $|d>$ states as atomic $d$-states but then they will not be the eigenstates of crystal Hamiltonian. We can safely assume $|\alpha>$'s to be the eigenfunctions of crystal Hamiltonian as they are not changed when metal is formed. The conduction band states satisfy the self-consistent Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V^{cr} (\vec{r}) \right] |\psi_k > = E |\psi_k >$$  \hspace{1cm} (2.2) 

The atomic $d$-states satisfy the following Schrödinger equation

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V^{at} (\vec{r}) \right] |d > = E_{d}^{at} |d >$$  \hspace{1cm} (2.3) 

Here, $V^{at} (\vec{r})$ is the atomic potential and $E_{d}^{at}$ is atomic $d$-state energy.

In order to account for the effect of $V^{cr} (\vec{r})$ on atomic $d$-states, we suppose that the crystal potential $V^{cr}$ may be related to atomic potential by

$$V^{cr} (\vec{r}) = V^{at} (\vec{r}) - \delta V (\vec{r})$$  \hspace{1cm} (2.4) 

Using Eq. (2.4) in Eq. (2.3), we get

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V^{at} (\vec{r}) \right] |d > = E_{d}^{at} |d > - \delta V (\vec{r}) |d >$$  \hspace{1cm} (2.5) 

Operating on both sides of Eq. (2.5) by $<d|$, we have,

$$<d| \left[ -\frac{\hbar^2}{2m} \nabla^2 + V^{cr} (\vec{r}) \right] |d > = E_{d}^{at} - <d| \delta V (\vec{r}) |d >$$
The left hand side of this equation is expectation value of crystal Hamiltonian. We denote this quantity by $\epsilon_d$

$$\epsilon_d = E_{d}^{at} - \langle d | \delta V (\vec{r}) | d \rangle$$ \hspace{1cm} (2.6)

or

$$E_{d}^{at} = \epsilon_d + \langle d | \delta V (\vec{r}) | d \rangle$$ \hspace{1cm} (2.7)

Using this value of $E_{d}^{at}$ in Eq. (2.5), we get,

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V^\sigma (\vec{r}) \right] | d \rangle = \epsilon_d | d \rangle + \langle d | \delta V (\vec{r}) | d \rangle | d \rangle$$

$$- \delta V (\vec{r}) | d \rangle$$

$$= (\epsilon_d - \Delta) | d \rangle$$ \hspace{1cm} (2.8)

where we have defined an operator $\Delta$ by

$$\Delta | d \rangle = | \delta V (\vec{r}) | d \rangle - |d\rangle < d | \delta V (\vec{r}) | d \rangle$$ \hspace{1cm} (2.9)

Eq. (2.8) represents the effect of crystal Hamiltonian on the atomic $d$ states.

Let us now introduce the pseudo-wave function defined by

$$\varphi = \sum_n B_n | \bar{k} + \bar{\gamma}_n \rangle$$ \hspace{1cm} (2.10)

Now substituting Eq. (2.1) in Eq. (2.2), we have

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V^\sigma \right) | \varphi \rangle + \sum_{\alpha} A_{\alpha} (E_{\alpha} - E) | \alpha \rangle$$

$$+ \sum_d C_d (\epsilon_d - E) | d \rangle - \sum_d C_d \Delta | d \rangle = E | \varphi \rangle$$ \hspace{1cm} (2.11)

The constant $A_{\alpha}$ can be obtained by operating on the left side of Eq. (2.11) with a core state $| \alpha \rangle$ and using the Hermitian property of Hamiltonian. We further assume that $\delta V (\vec{r})$ and hence $\Delta$ to be almost constant in the region of spread of core state. This leads us to

$$A_{\alpha} = - < \alpha | \varphi >$$ \hspace{1cm} (2.12)
In order to evaluate $C_d$ we multiply Eq. (2.11) by $<d\phi>$. We now assume strong localization of $d$-states. This assumption implies that $d$-states of neighbouring atoms do not overlap. This means that $d$-bands are only formed by the potential $\delta V(\vec{r})$. The result is,

$$C_d = -<d\phi> + \frac{<d\Delta|\varphi>}{\epsilon_d - E}$$  \hspace{1cm} (2.13)

Using $A_\alpha$ and $C_d$ in Eq. (2.11), we get

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + W\right]|\phi> = -\sum_d \frac{\Delta|d><d\varphi>}{\epsilon_d - E} = E|\phi>$$  \hspace{1cm} (2.14)

where, the transition metal pseudopotential $W$ is

$$W|\phi> = V_\sigma|\phi> + \sum_\alpha (E - E_\alpha)|\alpha><\alpha|\phi> + \sum_d (E - E_d)|d><d|\phi> + \sum \Delta|d><d\varphi>$$  \hspace{1cm} (2.15)

In Eq. (2.15), the first two terms on the right hand side are the same as found for simple metals. The presence of $d$-states has added three more repulsive terms: one through $d$-band energy $E_d$ and other two through $\Delta$. The matrix element of second term on the left hand side of Eq. (2.14) between plane wave states $|k>\psi$ and $|k + q>$ can be written as

$$-\sum_d <\vec{k} + q|\Delta|d><d|\Delta|\vec{k}>$$  \hspace{1cm} (2.16)

Since this expression contains a matrix element between the plane wave state $|k>\psi$ and $|d>$-state, the term

$$-\sum_d \frac{\Delta|d><d\Delta}{\epsilon_d - E}$$  \hspace{1cm} (2.17)

is called the hybridization potential. Treating Eq. (2.17) as hybridization potential allows us to speak of hybridization energy. Eq. (2.14) can be used to calculate total energy of a transition metal. A useful quantity that appears in the energy-expression which is based on second order perturbation theory is energy wave number characteristic. Based on Harrison's
theory, this is given by (for a monoatomic lattice) [Moriarty 1988]:

\[
F(q) = \frac{2\Omega_0}{(2\pi)^3} \left[ \int_{k<k_f} d^3k \left| \frac{\partial \rho_k}{\partial \Delta k} \right|^2 - \int_{k>k_f} \frac{d^3k}{(\Delta k)^2} \left( \sum_a \alpha_d \alpha_d^* + c.c. \right) \right.
\]

\[
+ \left( \sum_d \frac{\partial \alpha_d}{\partial \Delta k} \right)^2 \left( \sum_d \frac{\partial \alpha_d}{\partial \Delta k} \right)^2 \right] \left. \right] - \frac{4\pi\Omega_0}{q^4} \left( 1 - f_{xc}(\bar{q}) \right) \left| n_{sc}(\bar{q}) \right|^2
\]

\[
+ f_{xc} \left| n_{oh}(\bar{q}) \right|^2
\]

where

\[
\alpha_q = \langle \bar{k} + \bar{q}|W_0|\bar{k} \rangle
\]

\[
\alpha_d = \langle \bar{k}|\Delta|d \rangle
\]

\[
\alpha_{dq} = \langle d|\Delta|\bar{k} + \bar{q} \rangle
\]

\[
(\Delta k)^2 = k^2 - |\bar{k} + \bar{q}|^2
\]

\[
W_0
\]

and \( n_{sc} \) and \( n_{oh} \) are the Fourier transforms of screening and orthogonalization charge densities respectively. \( W_0 \) is the optimized pseudopotential which consists of the contributions from the self-consistent potential associated with the single ion site and the orthogonalization corrections for both the core and \( d \)-band states. The function \( f_{xc} \) accounts for exchange and correlation interactions. Apart from Harrison's paper, there are a number of other related works, in particular, those by Moriarty [1970, 1972a, 1972b, 1972c, 1973, 1979, 1974, 1977, 1982, 1986, 1988, 1990]. Moriarty also treats the \( d \)-orbitals as a separate group which automatically brings about the term like Eq. (2.17), so leaves one within the Harrison's scheme. Moriarty [1977, 1982] rederived the generalized pseudopotential theory of \( d \)-band metals using the self-consistent field equations of Kohn and Sham (1965) as the starting point. The basic features of the original theory were recovered but a number of important and unifying refinements were achieved. The total exchange and correlation potential was considered in the form of a constant plus a sum of overlapping, but structure independent intra-atomic potentials. This result, combined with his previously introduced zero-order pseudoatom technique of defining core and
\(d\)-states permitted an accurate first principles evaluation of all matrix elements entering the theory. Moriarty treated the structure dependence of the hybridization potential explicitly. This led to new second order terms in the total energy. Moriarty calculated the binding energy of \(Cu\) and several other simple \(d\)-band metals. It is interesting to note that in this paper first principles overlap interaction between ions was calculated. Moriarty (1988) extended the density functional formulation of generalized pseudopotential theory for empty and filled \(d\)-band metals to partially filled \(d\)-band metals. Within this formalism, a rigorous real space expansion of the bulk total energy was obtained in terms of widely transferable structure-independent inter-atomic potentials, including both central force pair interactions and angular force triplet and quadruplet interaction, (see also Moriarty (1990). Harrison and his coworkers (1983, 1984, 1987) have also attempted to obtain a general ion-ion potential for transition metals and rare earth metals. The expressions for the different contributions to the total energy of a transition metal are written up to second order in \(\Delta\). It is found that Coulomb terms cancel exactly. The remaining terms are calculated using atomic data so that the bulk properties are reproduced reasonably. From this total energy calculations the ion-ion interaction potential is written as

\[
v_{nl}(r) = v_{fe}(r) + v_{dd}(r) + v_{d}(r)
\]

(2.20)

Here \(v_{fe}(r)\) is effective two-body interaction between the ions screened by conduction electrons. This can be calculated by any appropriate "simple metal pseudopotential" [Heine-Abarenkov (1964), Aschroft empty core model (1968), Wallace's model (1968), etc.]. If one uses Thomas-Fermi approximation for the screening and Ashcroft empty core model for the bare ion potential, then

\[
v_{fe}(r) = \frac{Z_{s}^{2}e^{2}}{r} \cosh^{2} \left( k_{TF}r_{c} \right) \frac{e^{-k_{TF}r}}{r}
\]

(2.21)
where \( k_{TF} = \left( \frac{4k_F}{\pi a_0} \right)^{1/2} \) is Thomas-Fermi inverse screening length, \( r_c \) is effective core radius appearing in Ashcroft's model potential

\[
V_{\text{ion}}(r) = \begin{cases} 
0, & r < r_c \\
-\frac{Z_s e^2}{r}, & r > r_c
\end{cases}
\] (2.22)

where \( a_0 \) is Bohr radius, \( k_F \) is Fermi wave vector and \( Z_s \) gives the number of \( s \) valence electrons.

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

\[
\phi_{d\bar{d}}(r) = \sum_\vec{k} \frac{<d|\Delta|\vec{k}> <\vec{k}|\Delta|d'>}{E_d - E_{\vec{k}}}
\] (2.23)

Using atomic \( d \)-state wave functions and summing over \( \vec{k} \), the inter-ionic separation dependence of \( \phi_{d\bar{d}}(r) \) is given by

\[
\phi_{d\bar{d}m} = \eta_{d\bar{d}m} \left[ \frac{\hbar^2 r_d^3}{m^2 r^5} \right]
\] (2.24)

where \( r_d \) is radius of \( d \)-state wave function and

\[
\eta_{d\bar{d}m} = \begin{cases} 
-\frac{45}{\pi} & \text{for } m = 0 \\
\frac{30}{\pi} & \text{for } m = 1 \\
-\frac{15}{2\pi} & \text{for } m = 2
\end{cases}
\] (2.25)

Further, the effect of \( d \)-bands is included through rectangular model of density of \( d \)-band states as suggested by Friedel (1969). Retaining only the central integrals within the Friedel model for the \( d \)-bands, the averaged \( d - d \) overlap interaction is given by

\[
\phi_{dd}(r) = -Z_d \left( 1 - \frac{Z_d}{10} \right) \left( \frac{12}{n} \right)^{1/2} \frac{28.1 \hbar^2 r_d^3}{\pi m^2 r^5}
\] (2.26)

where \( n \) is number of nearest neighbours and \( Z_d \) stands for \( d \)-electron valency. There is also a contribution to the inter-ionic potential due to
s–d hybridization between the occupied and unoccupied d-states and the free electron states |\tilde{k}\rangle. The s–d hybridization modifies the d-charge in the occupied |d\rangle states which gives a change in the d-state occupation say by $\Delta Z_d$. This $\Delta Z_d$ is accompanied by an equal and opposite change 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\rangle states overlap through |\tilde{k}\rangle states, therefore, |d\rangle states are perturbed and are rendered non-orthogonal. An additional interaction arises due to overlap of perturbed |d\rangle states on the nearest neighbours. The first order calculations yield average overlap interaction as

$$\phi_d(r) = Z_d \frac{225.0 \hbar^2 r_d^6}{\pi^2 mr^8}$$

(2.27)

$\phi_d(r)$ has the effect of shifting the d-band centre. The discussion given above splits the $\phi(r)$ into $\phi_s^{(1)}(r)$ and $\phi_d^{(2)}(r)$ as follows:

$$\phi(r) = \phi_s^{(1)}(r) + \phi_d^{(2)}(r)$$

(2.28)

where

$$\phi_s(r) = \frac{p_1}{r} + \frac{p_2}{r} + \frac{p_3}{r}$$

(2.29)

$$\phi_d^{(2)}(r) = \frac{p_4}{r^5} + \frac{p_5}{r^8}$$

(2.30)

The coefficients $p_i$ are

$$p_1 = -\left(0.916Z_s^{4/3} + \alpha M Z_s^2\right)\left(\frac{8\pi}{3}\right)^{1/3}\sqrt{3}\frac{e^2}{4}$$

(2.31)

$$p_2 = 1.67\left(\frac{\hbar^2}{m}\right)\left(\frac{8\pi}{3}\right)^{2/3}Z_s^{5/3}$$

(2.32)

$$p_3 = \left(\frac{3\sqrt{3}\pi}{2}\right)e^2 c Z_s^2$$

(2.33)

$$p_4 = Z_d\left(1 - \frac{Z_d}{10}\right)(30.98)\sqrt{n_1}\left(\frac{\hbar^2}{m}\right)r_d^3$$

(2.34)

$$p_5 = 91.2Z_d\left(\frac{\hbar^2}{m}\right)r_d^6$$

(2.35)
Note that \( Z = Z_s + Z_d \). \( \alpha_M \) is Madelung constant (1.79186 for b.c.c., 1.79175 for f.c.c., 1.79168 for h.c.p.). McDonald and Taylor [1984] also calculated the ion-ion interaction for transition metals using a model \( d \)-band structure and found that the potential is not very sensitive to ionic configuration. These authors parametrized the ion-ion interaction for f.c.c. structure as

\[
\phi_i(r) = A \exp \left( -\frac{Br}{a} \right) \frac{a}{r} - \frac{C \cdot f_d}{\left[ 1 + \left( \frac{r}{r_t} \right)^2 \right]^5}
\]

where \( A, B, C \) and \( r_t \) are adjustable parameters, \( a \) is lattice constant and

\[
f_d = \frac{N_d (10 - N_d)}{(1 + \frac{N_d}{50})}
\]

Here \( N_d \) is the number of occupied \( d \)-states per spin and it is defined as

\[
\sum_d \theta (E_F - E_d) = N_d
\]

It is worth mentioning the work of Moriarty who has developed a first principle inter-atomic potential expansion of total energy suitable for transition metals [Moriarty (1972a, 1977, 1982, 1988, 1990)]. In the bulk elemental metal with atomic volume \( \Omega \), the total energy functional takes the form

\[
E_{\text{tot}} \left( \vec{R}_1, \ldots, \vec{R}_N \right) = E_0 (\Omega) + \frac{1}{2} \sum_{i,j} \phi_2 (t_{ij}) + \frac{1}{6} \sum_{i,j,k} \phi_3 (t_{ij}, k) + \frac{1}{24} \sum_{i,j,k,l} \phi_4 (t_{ij}, k, l)
\]

The leading volume term \( E_0 \) in this expansion includes all one-ion intra-atomic contributions to the total energy and already leads to a good description of transition metal cohesion in lowest order. The inter-atomic potentials \( \phi_2, \phi_3 \) and \( \phi_4 \) are given in terms of weak pseudopotential and \( d \)-state tight-binding and hybridization matrix elements coupling different sites and the series is rapidly convergent beyond three-ion interactions. As in the corresponding theory of non-transition metals [Moriarty (1977,
the inter-atomic potentials are volume dependent but structure independent and thus rigorously transferable at a given volume to all bulk structures, either ordered or disordered. At constant volume $\Omega$, the central force pair potential $\phi_2$ is a one-dimensional function of the ion-ion separation distance

$$R_{ij} = |\vec{R}_i - \vec{R}_j|$$

(2.37)

$$\phi_2 (ij) = \phi_2 (R_{ij}, \Omega)$$

The angular force triplet potential $\phi_3$ and quadruplet potential $\phi_4$ are, respectively, the three- and six-dimensional functions

$$\phi_3 (i,j,k) = \phi_3 (R_{ij}, R_{ij}, R_{ik}, \Omega)$$

(2.38)

and

$$\phi_4 (i,j,k,\ell) = \phi_4 (R_{ij}, R_{ij}, R_{ik}, R_{ik}, R_{ij}, \Omega)$$

(2.39)

In the full first principles Generalized Pseudopotential Theory (GPT), the potentials $\phi_2$, $\phi_3$ and $\phi_4$ are all nonanalytic functions with long-range oscillatory tails. Also, unlike $\phi_2$, the multi-dimensional functions $\phi_3$ and $\phi_4$ cannot be readily tabulated for application purposes. This makes the application of the theory more difficult. For the central transition metals the multi-ion potentials are essential to an accurate description of material properties. Keeping this fact in mind Moriarty has developed a simplified model transition metal GPT [see abstract after 1990] in which $\phi_3$ and $\phi_4$ are approximated by analytic short range forms that retain the dominant physics of the full theory. In the model GPT the troublesome long range oscillatory tails of $\phi_2$, $\phi_3$ and $\phi_4$ are neglected. These tails arise primarily through indirect hybridization interactions. However, the first principles GPT calculations show that these tails interfere destructively in the calculation of material properties. As in the first principles GPT, the two-ion $d$ state orthogonality contributions are absorbed into a repulsive hard core type potential. The three and four ion contributions from non-orthogonality matrix elements are neglected. Next, canonical $d$-bands are
introduced to express the remaining $\Delta_{dd'}$ matrix elements analytically.

In a pure canonical $d$-band description

$$\Delta_{dd'}^{\nu c}(R_{ij}) = \alpha_m \left( \frac{R_{ws}}{R_{ij}} \right)^5$$  \hspace{1cm} (2.40)

Here $5$ corresponds to $2\ell + 1 = 5$ for $\ell = 2$. $R_{ws}$ is Wigner-Seitz radius. $\alpha_m$ are constants. Eq. (2.40) can be generalized by replacing $5$ by $p$ where $p$ is material dependent constant. Finally, Moriarty arrives at the following expression for two-ion interaction

$$\phi_2 = \phi_2^{sp}(r) + \phi_2^{hc}(r) + \phi_2^d(r)$$  \hspace{1cm} (2.41)

where $\phi_2^{sp}$ and $\phi_2^{hc}$ are the components of the first principles theory.

$$\phi_2^d(r) = \phi_a [f(r)]^4 - \phi_b [f(r)]^2$$

$$\phi_a \left( \frac{r_0}{r} \right)^{4p} - \phi_b \left( \frac{r_0}{r} \right)^{2p}$$  \hspace{1cm} (2.42)

where $r_0 \equiv 1.8R_{ws}$. The quantities $\phi_a$ and $\phi_b$ are material related constants which depend primarily on $d$-band filling. Generally, as the theory shows $\phi_b \gg \phi_a$. Eq. (2.41) represents the total two-ion pair potential. Moriarty [1990] has also developed the explicit expressions for 3-ion and 4-ion interaction potentials which we do not reproduce here. In an another development of pseudopotential theory, Animalu [1973] applied the concept of quantum defects to transition metals and extended the work of Abarankov, Heine and Animalu 1965, 1964, 1965] for simple $s - p$ bonded metals.

In this work Animalu generalized the quantum defect law and elements having $Z$ (valence) $\geq 2$ from an extensive study of the spectroscopic data of first six rows of the periodic table. This quantum defects law states that the energy levels $E_{nl}$ of a single electron in the field of the positive ions of elements having the same inert gas core e.g., the elements of the
isoelectronic sequence $Li^{+}$, $Be^{2+}$... $F^{7+}$ which are given (in the Heine-Abarenkov model potential method) by the spectroscopic term value of the ion plus one electron i.e. by the term values of $Li^{+}$, $Be^{2+}$...$F^{6+}$ obey the relation

$$E_{nt} = -\frac{Z^2}{(n - \delta_{nt})^2} + \Delta_{nt}, \ z \geq 2$$

for the same quantum defects ($\delta_{nt}$, $\Delta_{nt}$). The old quantum defect ($\delta_{nt}$) and the new quantum defect $\Delta_{nt}$ (equivalent to an atomic core shift) thus represent the deviation of the atomic potential of a given inert gas configuration from a Coulombic potential due to a nuclear charge $Z|e|$. On the basis of this empirical law, the parameters of a transition metal model potential of the Heine-Abarenkov type are adjusted to the energies.

$\epsilon_{nt} \equiv E_{nt} - \Delta_{nt}$ were calculated for all 30 group B (excepting rare earth) metals of the periodic table. It was found that the $\ell = 2$ model potential parameter $A_2$ reflects the Ziman-Heine-Hubbard resonance model of $s-d$ hybridization through its strong energy dependence of the form $(\epsilon - \epsilon_{3d})^{-1}$ for the $3d$ series and similarly for the $4d$ and $5d$ series. The main task in this work is to set up a model potential to simulate the information contained in the quantum defects ($\delta_{nt}$, $\Delta_{nt}$) about the nature of the true atomic potential. Animalu defined the transition metal model potential (TMMP) of the Heine-Abarenkov type as follows:

$$V_m = -\sum_{\ell} A_\ell P_\ell \text{ for } r < R_m$$

$$= -\frac{Z}{r} \text{ for } r > R_m$$

(2.44)

Here $A_\ell$ = well depth for $\ell = \ell$ for given $R_m$, $P_\ell$ = projection operator that picks out the $\ell$th angular momentum component of an incident one electron wave function, and $Z$ = chemical valence of the isolated ion of the metal.

As $\Delta_{nt}$ represents the core shift, the true one electron atomic potential for
the electronic state \((n, \ell)\) can be written as

\[
V_{n\ell}(r) = V_{nt}(r) + \frac{1}{2}\Delta_{n\ell}(au) \tag{2.45}
\]

The true radial wave equation is,

\[
\left[ -\frac{1}{2}\frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{r^2} + V_{n\ell}(r) \right] P_{n\ell}(r) = \frac{1}{2}(E_{n\ell} - \Delta_{n\ell}) P_{n\ell}(r) \tag{2.46}
\]

where \(V_{n\ell}\) is Coulombic for \(r > r_c\) (the ion core radius). Here \(\tilde{V}_{n\ell}(r)\) is the model potential of Eq. (2.44). This potential is so adjusted that it generates the eigen value \(\epsilon_{n\ell} = E_{n\ell} - \Delta_{n\ell}\) exactly. By matching the logarithmic derivatives of pseudowave functions at \(R_m\), one obtains an eigen value problem for \(X\):

\[
\frac{X_{2\ell-1}(X)}{j_\ell(X)} - \ell = 0^D \ell (ZR_m) + \gamma(N, \ell) 1^D \ell (ZR_m) \tag{2.47}
\]

where

\[
X = R_m (2A_\ell - |\epsilon|)^{1/2} = (ZR_m) \left( \frac{2A_\ell}{Z^2} - \frac{|\epsilon|}{Z^2} \right)^{1/2} \tag{2.48}
\]

\(0^D \ell\) and \(1^D \ell\) are the Coulomb wave functions which are, respectively, regular and irregular at the origin. \(0^D \ell\) and \(1^D \ell\) are their derivatives. \(D^\ell = \rho \left( \frac{d\rho}{dr} \right)\), \(\rho = Zr\). \(j_\ell(X)\) are spherical Bessel's functions. The ratio \(\gamma(N, \ell)\) of the two Coulomb wave functions is the usual one that involves the quantum defect \(\delta_{n\ell}\) via the effective quantum number \(N = n - \delta_{n\ell}\) in QDM:

\[
\gamma(N, \ell) = \frac{\Gamma(N - \ell) \tan \pi(N - \ell - 1) N^{2\ell+1}}{\Gamma(N + \ell + 1)} \tag{2.49}
\]

The numerical solution of Eq. (2.47) showed \(A_0\) and \(A_1\) vary smoothly with energy through the atomic term values, while \(A_2\) goes to infinity at \(E_{4d}\) and \(E_{5d}\) but not at the expected position of the \(d\)-band resonance, \(E_{3d}\) for \(Cu\).

Taking core shift into account, it can be shown that

\[
A_2(\epsilon) \propto (\epsilon - \epsilon_{3d})^{-1} \tag{2.50}
\]

in the neighbourhood of \(3d\) level for \(Cu\). Thus Eq. (2.50) provides an empirical evidence for the resonance model [Ziman (1965), Heine (1967),...
Hubbard (1967) of transition metal $d$ bands in the framework of the pseudopotential theory [Harrison (1969)]. Animalu has shown that the key distinction between the transition and simple metal model potential theories is provided by the size of the core shift. The analysis of the numerical solutions of Eq. (2.47) showed that the pertinent form of the TMMP is

$$V_m(r) = -C - (A_0 - C) P_0 - (A_1 - C) P_1 - (A_2 - C) P_2 \quad \text{for } r < R_m$$

$$= -\frac{Z}{r} \quad \text{for } r > R_m$$

(2.51)

where $c = \frac{Z}{R_m}$.

In view of Eq. (2.50), the potential

$$V_T(r) = -(A_2 - C) P_2 \quad \text{for } r < R_m$$

$$= 0 \quad \text{for } r > R_m$$

(2.52)

corresponds to Harrison's hybridization or resonance term. Animalu has calculated the model parameters for 30 elements. He has also made extensive calculations of various properties of the transition metals. His studies on phonon spectra, liquid metal resistivity and energy bands in the local pseudopotential approximation showed that model potential approach leads to reasonable agreement between theory and experiment. For the sake of completeness, we give below an explicit expression for the screened model potential form factor $V(q)$. In the local screening approximation

$$V(q) = \frac{V^{(b)}(q)}{\epsilon(q)}$$

(2.53)

where

$$V^{(b)}(q) = \langle \vec{K}_f + \vec{q}|(V_m + V_{oc} + V_{cc})|\vec{K}_f \rangle$$

$$\equiv F(\vec{K}_f, \vec{K}_f + \vec{q}) + B(q)$$

(2.54)

where $V_m$ is model potential defined by Eq. (2.51). $V_{oc}$ and $V_{cc}$ are the usual
orthogonalization and correlation corrections [Animalu and Heine (1965)].

\[ B(q) = -\frac{8\pi}{\Omega q^3} \left[ \sin(qR_m) - qR_m \cos(qR_m) \right] \]
\[ -\frac{8\pi Z}{\Omega q^3} \cos(qR_m) + \left( \frac{4\pi Z e^2}{\Omega q^3} - \frac{24\pi Z a_{ef}}{\Omega q^3(qR_m)^3} \right) \]
\[ \times \left[ \sin(qR_c) - qR_c \cos(qR_c) \right] \]

(2.55)

For \( |\vec{k}_f + \vec{q}| = k_f \),

\[ F(\vec{K}_f, \vec{K}_f + \vec{q}) = -4\pi \Omega^{-1} R_m^3 (A_0 - c) \left\{ [j_0(x)]^2 - x^{-1} \cos x j_1(x) \right\} \]
\[ -12\pi \Omega^{-1} R_m^3 (A_1 - c) \left\{ [j_1(x)]^2 - j_0(x)j_2(x) \right\} P_1(\cos \theta) \]
\[ -20\pi \Omega^{-1} R_m^3 (A_2 - c) \left\{ [j_2(x)]^2 - j_1(x)j_3(x) \right\} P_2(\cos \theta) \]

(2.56)

where,

\[ x = k_f R_m \]
\[ \cos \theta = \left( 1 - \frac{q^2}{2k_f^2} \right) \]
\[ P_1(\cos \theta) = \cos \theta \]
\[ P_2(\cos \theta) = \frac{1}{2} (3 \cos^2 \theta - 1) \]
\[ j_0(x) = x^{-1} \sin x \]
\[ j_1(x) = x^{-2} \sin x - x^{-1} \cos x \]
\[ j_2(x) = (3x^{-3} - x^{-1}) \sin x - 3x^{-2} \cos x \]
\[ j_3(x) = 5x^{-1}j_2(x) - j_1(x) \]

For \( |\vec{K}_f + \vec{q}| \neq K_f \),

\[ F(\vec{K}_f, \vec{K}_f + \vec{q}) = -\frac{8\pi R_m^3}{n(x^2-y^2)} \left[ xj_1(x)j_0(y) - yj_1(y)j_0(x) \right] \]
\[ -\frac{24\pi R_m^3 (A_1 - c)}{n(x^2-y^2)} \times [xj_2(x)j_1(y) - yj_2(y)j_1(x)] \times P_1(\cos \theta') \]
\[ -\frac{40\pi R_m^3 (A_2 - c)}{(x^2-y^2)} \times [xj_3(x)j_2(y) - yj_3(y)j_2(x)] \times P_2(\cos \theta') \]

(2.57)

where,

\[ y = \frac{|\vec{K}_f + \vec{q}| R_m}{x^2 + y^2 - (qR_m)^2} \]
\[ \cos \theta' = \frac{x^2 + y^2 - (qR_m)^2}{2xy} \]

(2.58)

(2.59)

The dielectric function \( \epsilon(q) \) is given by

\[ \epsilon(q) = 1 + [1 - f(q)] \left( \frac{4\pi Ze^2}{\Omega q^3} \right) \chi \left( \frac{q}{2k_f} \right) \]

(2.60)
where

\[ \chi(X) = \left( \frac{3E_F}{2} \right) \left[ \frac{1}{2} + \frac{1}{4} \left( \frac{1 - X^2}{X} \right) \ln \left| \frac{1 + X}{1 - X} \right| \right] \]  

\[ E_F = \frac{\hbar^2 k_F^2}{2m^*} \]  

\[ e^* = (1 + \alpha_{eff}) e^2 \]

and \( f(q) \) = exchange and correlation correction to the dielectric function. Here \( V(q) \) is in Ryd when all entries are in atomic unit except \( |E_c| \) which is in Ryd. In atomic units \( e = \hbar = m = 1, c = \frac{Z}{\hbar_m} \). Dagens [1975] noted that Animalu's resonant form of model potential was not quite correct. Also, Animalu did not give a consistent theory of screening. Dagens [1975] proposed a different resonant model potential in which consistent theory of screening was also given. The ionic model potential proposed by Dagens has the form

\[ v_0(E') = W_0(E') + v_{res}(E') \]  

\[ = W_0(E') + \frac{U}{E' - \delta} \]

where,

\[ E' = E - E_0 \]

Here \( E_0 \) is bottom of the valence band. \( W_0 \) is Heine-Abarenkov [1964] model potential. \( v_{res} \) is the resonant part \( \frac{U}{E' - \delta} \) with \( U \) acting only on \( d \) states and separable in each \( m \) channel. Its matrix element normalized in the atomic cell is written as [Heine 1967]

\[ U(qk) = 4\pi A_d \gamma(k') \gamma(k) \sum_m Y_{2m}(\hat{k}') Y_{2m}(\hat{k}) \]

with

\[ \hat{k}' = \hat{k} + \hat{q} \]

\[ \gamma(k) = \frac{j_2(x_0)}{1 - \left( \frac{4\pi k}{x_0} \right)^2} \]

\( x_0 = 5.76346 \) is the first zero of spherical Bessel's function \( j_2(x) \).

In the practical application of this model Dagens took \( W_0 \) as a local and energy independent optimized potential:

\[ W_0(q) = -\frac{4\pi Ze^2}{\Omega_0 q^2} \sin qR_0 \]
The parameter $R_0$ for three noble metals was fitted to the $L_2 - X'_1$ band gap using lowest order perturbation. For Ca, $R_0$ was taken equal to the mean value of the optimized $\ell = 0$ and $\ell = 1$ model radius calculated by Ese and Reissland [1973]. $R_d$ was taken as $R_0$. The resonant potential parameters were determined as described by Dagens [1975, 1976]. Here $R_d$ has been so selected that the so called overlap inter-ionic potential of the OPW formulation [Moriarty 1972a], which is a consequence of the overlap of the ionic OPW pseudopotentials, does not appear in the present theory as a separate contribution. For the sake of convergence, it was found necessary to normalize the energy parameter $\delta(E)$. Denoting the renormalized energy parameter by $\tilde{\delta}(E)$ one has to write renormalized resonant potential as follows:

$$
\tilde{v}_{res} = \frac{u}{E - \delta(E)}
$$

(2.69)

$\tilde{\delta}$ was determined so that $\tilde{v}_{res} \left( E_k^{(0)} \right)$ is equal to the reaction matrix relative to $v_{res} \left( E_k^{(0)} + \Delta E_k \right)$. The renormalized screened model potential is obtained as

$$
\tilde{v} \left( \vec{k}, \vec{q}, E \right) = W \left( \vec{q}, \vec{k} \right) + \frac{u \left( \vec{q}, \vec{k} \right)}{E - \delta(E)}
$$

(2.70)

with

$$
W \left( \vec{q}, \vec{k} \right) = W_0 \left( \vec{q}, \vec{k} \right) + \frac{I(q)n_{sc}(q)}{Q_0}
$$

(2.71)

The last term represents the contribution of the screening density. $I(q)$ is known as interaction function and reduces to $\frac{4\pi e^2}{q^2}$ in the Hartree approximation. $n_{sc}$ is the pseudo-atom screening density.

$$
I(q) = \frac{4\pi e^2}{q^2} + X(q)
$$

(2.72)

where, $X(q)$ often denoted as $\frac{4\pi^2 Q(q)}{q^2}$ includes all the exchange and correlation contributions. The $X(q)$ leading to the dielectric function of Geldard and Taylor [1970] was used. The energy wave number characteristic $F(q)$
is given by

\[ F(q) = \phi_a(q) + \phi_b(q) + \phi_c(q) \]

\[ + \frac{f(q)}{\alpha_0} \left[ n_{dp}^2(q) - n_{ps}^2(q) \right] \]

The expressions for \( \phi_a, \phi_b \) and \( \phi_c \) are given by Dagens [1977]. \( n_{dp} \) is depletion hole charge density. \( n_{ps} \) is Fourier transform of \( s-p \) charge density. Dagens applied the model to Cu, Ag, Au and Ca to compute inter-atomic potentials, binding energy, phase stability and elastic constants with reasonable success. The orthogonalized plane wave (OPW) concept underlying the pseudopotential method was used to derive "first principles" pseudopotentials from atomic calculations. These potentials are generally "hard core" in character, that is strongly repulsive at the origin [Melius and Goddard (1974), Zunger and Cohen (1978)]. The resulting wave functions generally exhibit the correct shape outside the core region; however they differ from the real wave functions by a normalization factor. Hamann et al. [1979] have developed a scheme by which the normalization and hard core problems can be solved simultaneously. This scheme also maximizes the range of systems in which a pseudopotential gives accurate results. This method permits the potential to be intrinsically "soft core" with a continuous range of compromise between potential strength and the "core radius" \( r_c \). This scheme of constructing pseudopotential is as follows:

1. First, an \textit{ab initio} self-consistent full core atom calculation via a Herman-Skillman like program is carried out. This program uses a local approximation for the exchange and correlation potential. This program generates the self-consistent potential \( V(r) \) and \( u_e(r) \) defined as \( r \) times the valence wave function.

2. Then a pseudopotential is constructed from \( V(r) \):

\[ V_{\ell}^{ps} = \left[ 1 - f \left( \frac{r}{r_{\ell}} \right) \right] V(r) + c_\ell f \left( \frac{r}{r_{\ell}} \right) \]
which converges to $V(r)$ for $r > r_{\text{cl}}$. Here $F(x)$ is the cut off function

$$x^{\frac{1}{n}} \to f(x) \to 0$$

$$x^{\frac{1}{n}} \to f(x) \to 1 \text{ as fast as } x^3$$

For each $\ell$, the cut off radius $r_{\text{cl}}$ is typically 0.5 to 1.0 times the radius $r_{\text{me}}$ of the outermost peak of $u_{\ell}$.

3. Now, $V_{\ell}^{p}$ is used in the radial Schrödinger equation and $C_{\ell}$ of the above equation is so adjusted that one gets nodeless wave function $W_{1\ell}$ with eigen value equal to the original eigenvalue $\epsilon_{\ell}$.

4. Now pseudo-wave function $W_{1\ell}$ is modified to $W_{2\ell}$ by

$$W_{2\ell}(r) = \gamma_{\ell} \left[ W_{1\ell}(r) + \delta_{\ell} g_{\ell} \left( \frac{r}{r_{\text{cl}}} \right) \right]$$

where $g_{\ell}(x)$ cuts off to zero for $x > 1$ and behaves as $x^{\ell+1}$ for small $x$. The chosen asymptotic behaviour of $f(x)$ and $g(x)$ guarantees the potential to be finite at the origin.

$\gamma_{\ell}$ can be obtained from

$$\gamma_{\ell} W_{1\ell}(r) \to r > r_{\text{c}} U_{\ell}(r)$$

$\delta_{\ell}$ is the smaller solution of the quadratic equation resulting from the condition that $W_{2\ell}$ be normalized.

$$\gamma_{\ell}^2 \int_{0}^{\infty} \left[ W_{1\ell}(r) + \delta_{\ell} g_{\ell} \left( \frac{r}{r_{\text{cl}}} \right) \right]^2 dr = 1$$

5. The final pseudopotential $V_{2\ell}^{p}$ producing the nodeless eigen function $W_{2\ell}$ at eigen value $\epsilon_{\ell}$ is now found by inverting the radial Schrödinger equation.

6. The valence pseudocharge density is found with the use of $W_{2\ell}$. The Coulomb and exchange correlation potentials due to this density are
then calculated and subtracted from each $V_{2d}^{ps}$. Analytical expressions containing few parameters can be fitted to the numerical potential functions. The choice of $f(x)$ and $g(x)$ of the following form has been found to be useful:

$$
\begin{align*}
    f(x) &= \exp(-x^4) \\
    g(x) &= x^{\ell+1} \exp(-x^4)
\end{align*}
$$

Interatomic potential functions play a fundamental role in determining the lattice mechanical properties of a substance. Many workers in early years have used the empirical potential function e.g. Morse function. Such functions can also be constructed by using the pseudopotential theory. Onwuagba and Animalu [1981] have reported a semi-empirical evidence that the local field correction due to $s-d$ interaction in the lattice dynamics of vanadium may be simulated by an attractive short range potential of the Born-Mayer type which tends to cancel or "screen" the usual repulsive Born-Mayer potential. They found that such an attractive short range potential led to a more detailed understanding of the occurrence of soft modes in the phonon spectrum of vanadium. Inspired by the above mentioned study Onwuagba used a generalization of the pseudopotential method to calculate contribution to inter-atomic potential in $d$-band transition metals due to $s-d$ interaction. To understand this, let us consider total inter-atomic potential energy of a transition metal containing $N$ transition metal ions of chemical valence ($Z = Z_s + Z_d$). Let $s$-electron and $d$-electron charge densities be $\rho_s$ and $\rho_d$ respectively. $\rho = \rho_s + \rho_d$. The interactions of these charge densities with positive ions are denoted by $V_s$ and $V_d$. $V = V_s + V_d$. The potential energy of the system is [Animalu (1977)]

$$
\Phi \left( \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N \right) = \sum_{i>j} (Ze)^2 / R_{ij}
+ \int \sum_{i>j} \rho \left( \vec{r} - \vec{R}_i \right) V \left( \vec{r} - \vec{R}_j \right) d^3r
= \Phi_0 + \Phi'
$$

(2.74)

where, $R_{ij} = |\vec{R}_i - \vec{R}_j|$. The second term represents the indirect ion-ion
interaction via the polarization field of the $s$ and $d$-electrons, and may be rewritten as a sum of two diagonal parts $\Phi'_{ss}$ and $\Phi'_{dd}$ and two off-diagonal parts, $\Phi'_{sd}$ and $\Phi'_{ds}$ as follows:

$$
\Phi' = \Phi'_{ss} + \Phi'_{dd} + \Phi'_{sd} + \Phi'_{ds}
$$

(2.75)

where,

$$
\Phi'_{nm} = \int \sum_{i>j} \rho_n (\vec{r} - \vec{R}_i) V_m (\vec{r} - \vec{R}_j) d^3r
$$

(2.76)

\( n, m = s, d \)

Since the $s$-electron is nearly free the charge density $\rho_s (\vec{r} - \vec{R}_a)$ associated with $Z_s$, the $s$-electrons of the $i^{th}$ atom may be replaced by a $\delta$-function, so that

$$
\rho_s (\vec{r} - \vec{R}_a) = Z_s (\vec{r} - \vec{R}_a)
$$

(2.77)

For $d$-electrons, we put

$$
\rho_d (\vec{r} - \vec{R}_a) \sum \psi_d^*(-\vec{r} - \vec{R}_a) \cdot \psi_d (\vec{r} - \vec{R}_a)
$$

(2.78)

and relate $V_d$ and $\rho_d$ by Poisson's equation

$$
\nabla^2 V_d (\vec{r} - \vec{R}_a) = -4\pi e^2 \rho_d (\vec{r} - \vec{R}_a)
$$

(2.79)

whose solution is

$$
V_d (\vec{r} - \vec{R}_a) = -4\pi e^2 \int \frac{\rho_d (\vec{r} - \vec{r} + \vec{R}_a)}{|\vec{r} - \vec{r} + \vec{R}_a|} d^3r'
$$

(2.80)

Then,

$$
\Phi'_{sd} = Z_s \int \delta (\vec{r} - \vec{R}_a) \sum_j V_d (\vec{r} - \vec{R}_j) d^3r
$$

(2.81)

Considering the above formalism and taking hydrogenic wave functions for $d$-electrons, Onwuagba has shown that contribution to inter-atomic potential due to $s - d$ hybridization interaction has the following form:

$$
\Phi' (\vec{R}_1, .. \vec{R}_N) = B \sum_{i>j} e^{-(i\vec{R}_a - \vec{R}_j)/\gamma}
$$

(2.82)
In practical calculations, the parameter $B$ comes out to be negative and hence this interaction is attractive in nature. An another important method of extracting inter-atomic pair potential is due to Daw and Baskes [1983, 1984]. This method is known as "embedded atom" method. This method is based on the quasiatom [Stott and Zaremba (1980)] or effective medium theory [Norskov (1982)]. In the embedded atom method each atom in a solid is viewed as an impurity embedded in a host comprising all the other atoms. The total energy of a solid is written (based on quasiatom concept) as

$$E_{tot} = \sum F_i (\rho_{h,i})$$  \hspace{0.5cm} (2.83)

where $F_i$ is the embedding energy, $\rho_{h,i}$ is the density of the host at the position $R_i$ but without atom $i$ and the total energy is the sum of the individual contributions. Equation (2.83) would lead to unrealistic properties of solid if one assumes extreme locality or complete uniformity of charge density. A complete uniform positive background is also not a good assumption. In fact, a real solid differs from jellium in that the charge densities are non-uniform. Also, this equation neglects the core-core repulsion. The correction for core-core repulsion is assumed here to take the form of a short ranged pairwise repulsion between the cores. The resulting total energy is, then, given by

$$E_{tot} = \sum F_i (\rho_{h,i}) + \frac{1}{2} \sum_{i \neq j} \phi_{ij} (R_{ij})$$  \hspace{0.5cm} (2.84)

where, $\phi_{ij}$ is the short range pair potential and $R_{ij}$ is the distance between atom $i$ and $j$. If we make a further simplification by assuming that the host density $\rho_{h,i}$ is closely approximated by a some of the atomic densities ($\rho^a$) of the constituent, i.e.

$$\rho_{h,i} = \sum_{j \neq i} \rho^a_j (R_{ij})$$  \hspace{0.5cm} (2.85)

then the energy will be a simple function of the positions of the atoms. (Here $\rho^a_j$ is the contribution to $\rho_{h,i}$ from atom $j$ where $\rho_{h,j}$ is the total host
electron density at atom \( j \). Using Eq. (2.84), ground state properties of a solid can be calculated. The function \( \phi_{ij} \) is assumed to have the form:

\[
\phi_{ij}(r) = \frac{Z_i(r)Z_j(r)}{r}
\]  

(2.86)

Here \( Z_{i,j} \) are effective charges of the atoms \( i \) and \( j \).

For each element we need \( F(\rho) \) and \( Z(r) \), the Clementi's atomic densities \( \rho^a(r) \) [1974] and the quantity \( N_s \):

\[
\rho^a(r) = N_s \rho^a_s(r) + (N - N_s) \rho^a_d(r)
\]

(2.87)

Here, \( N_s \) is an empirical parameter which corresponds to the s-like content of the atomic density. \( N \) is the total number of outer electrons. For a homo-nuclear crystal, because all the atoms are identical, we have

\[
F = F_t, \quad \phi = \phi_{ij} \quad \text{and} \quad \rho = \rho^a_j
\]

(2.88)

We can define \( \bar{\rho} \) to be the density at equilibrium

\[
\bar{\rho} = \sum_m \rho(a_m)
\]

(2.89)

where \( a_m \) are the distances between neighbours and the sum is over neighbours. Also, we define,

\[
\bar{\phi} = \sum_m \phi(a_m)
\]

(2.90)

The lattice constant is given by the equilibrium condition

\[
A_{ij} + F'(\bar{\rho}) V_{ij} = 0
\]

(2.91)

where

\[
A_{ij} = \frac{1}{2} \sum_m \phi'_m a_m a_{jm} / a_m
\]

(2.92)

\[
V_{ij} = \sum_m \rho'_m a_m a_{jm} / a_m
\]

(2.93)

where \( a_{jm} \) is the \( j \)th component of the position vector to the \( m \)th neighbour

\[
\phi'_m = \left[ \frac{d\phi(r)}{dr} \right]_{r=a_m}
\]

(2.94)
The total energy of the configuration of atoms is written as

\[ U_{\text{tot}} = U_N + \frac{1}{2} \sum_{ij} V(R_{ij}) \]

\( U_N \) is the \( N \)-body term and the second term is a conventional pair potential summation. The \( N \)-body term has the form:

\[ U_N = -A \sum_i \left( \sum_j \phi(R_{ij}) \right)^{1/2} \]

This represents the cohesion in the manner of a second moment approximation to the tight binding band energy, which gives rise to a cohesive
energy arising as the square root of atomic coordination. The above energy functions were parametrized in a purely empirical way by (FS). Thus,

\[ \phi(r) = \begin{cases} (r - d)^2 & r < d \\ 0 & r > d \end{cases} \]

\[ V(r) = \begin{cases} (r - c)^2 (C_0 + C_1 r + C_2 r^2) & r < c \\ 0 & r > c \end{cases} \]

The cut-offs \( d \) and \( c \) were taken to lie between second and third neighbour separations. These and other parameters \( A, C_0, C_1 \) and \( C_2 \) were fitted to the experimental cohesive energy, lattice parameter and three elastic constants. The remaining sixth degree of freedom in the fitting was used to ensure that the unrelaxed vacancy formation energy was in the range of observed values. This model was improved by Ackland and Thetford [1986]. These authors took the core to be of short range. The core was fitted to the forces, rather than the energies. The forces were deduced from electron gas potential. In order to ensure a smooth pressure volume relation, it was necessary that the added core function and its derivatives go to zero at the cut-off. The potential is designed to be most accurate in the lower energy range, near to equilibrium separations, where the atoms are most likely to be found. These considerations lead to the following form of \( V(R_{ij}) \)

\[ V(R_{ij}) = V_{ps}(R_{ij}) + B (b_0 - R_{ij})^3 e^{-\alpha R_{ij}} \]

The parameters \( B \) and \( \alpha \) were determined from fitting in the region 0.4 < \( \frac{R_{ij}}{b} \) < 1.0. \( b_0 \) is nearest neighbour distance. Ackland et al. [1988] have examined the validity of square root function in the context of second moment tight binding model.

In addition to the above mentioned approaches, some other efforts on the line of first principles to account for lattice dynamical properties of metals and alloys have also been made. The microscopic theories of lattice
dynamics were first developed by Baym [1961] and Cochran [1963]. In these theories of lattice dynamics, screening of ion-ion interaction through conduction electrons is a central phenomenon. Hence, these theories are centred around general formulations of dielectric screening.

To understand the phenomenon of screening, let us consider the original potential $V_{\text{ion}}$ of a certain ion and $V_{\text{scr}}$ the screening potential due to the electrons. Note that screening potential arises out of change in the original electron density due to ionic potential. Then, crystal potential

$$V_{\text{cr}} = V_{\text{ion}} + V_{\text{scr}}$$  \hspace{1cm} (2.96)

This total potential acts on the electrons and in turn requires screening. The resultant new potential also requires screening and so on. It will be understood that at each successive iteration the screening has a progressively smaller effect on the potential until the potential becomes self-consistent. We need to express $V_{\text{scr}}$ in terms of the final result of screening $V_{\text{cr}}$. We denote the density of the screening electrons as $\rho_{\text{scr}}$ and for simplicity we use operator notation. At every iteration

$$V_{\text{scr}} = \hat{A} \rho_{\text{scr}}$$  \hspace{1cm} (2.97)

where $\hat{A}$ is an operator. This equation expresses the obvious fact that a screening potential arises from the non-uniformity of the electron gas density. On the other hand, this departure from the mean is caused by the total crystal potential $V_{\text{cr}}$. In a general form this may be written

$$\rho_{\text{scr}} = \hat{B} V_{\text{cr}}$$  \hspace{1cm} (2.98)

where the operator $\hat{B}$ is to be found later. The screening potential can thus be expressed in terms of its action

$$V_{\text{scr}} = \hat{A} \hat{B} V_{\text{cr}}$$  \hspace{1cm} (2.99)
We now suppose that the iterative process has been carried through to self-consistency, i.e. \( V^{\sigma} \) coincides with the crystal potential given by the sum of the original potential and the corresponding screening potential. We may then consider that \( V^{\sigma} \) of Eq. (2.96) coincides with its counterpart in Eq. (2.99). Finally,

\[
V^{\sigma} = V^{\text{ion}} + \hat{A} \hat{B} V^{\sigma} \tag{2.100}
\]

(Note: There is another approach in which a model is used to construct \( V^{\text{scr}} \) [Yastrebov and Katsnelson (1987)].)

Let us introduce the operators

\[
\hat{\epsilon} = 1 - \hat{A} \hat{B} \quad \text{and} \quad \hat{\epsilon}^{-1} = \left(1 - \hat{A} \hat{B}\right)^{-1}
\]

Then,

\[
\hat{\epsilon} V^{\sigma} = V^{\text{ion}} \quad \text{and} \quad V^{\sigma} = \hat{\epsilon}^{-1} V^{\text{ion}} \tag{2.102}
\]

The operator \( \hat{\epsilon} \) is called the dielectric operator. The dielectric formalism given above is applicable to both potentials and pseudopotentials, since there are no restrictions on the strength of the original potential. However, the computational difficulties encountered in dealing with \( \hat{\epsilon} \) necessitate small parameter expansions. In the linear response approximation \( \hat{\epsilon} \) turns out to be a tensor. Its inverse space form is given by

\[
\epsilon(q, \xi) = \delta_{q\xi} - g(q, \xi)
\]

Here \( g(q, \xi) \) is Fourier transform of \( g(\vec{r}, \vec{r}') \) which is screening potential at \( \vec{r} \) due to a unit potential at \( \vec{r}' \). The quantum mechanical description of dielectric tensor has been given by many authors [Venkatesan et al. (1975), Sham and Ziman (1965), Sinha (1980)]. In such description, generally electron-electron interaction appearing in the self-consistent Schrödinger equation is included in the Hartree approximation and the linear response to the external field is accounted for. The electronic wave functions are
calculated in first order in pseudopotential and screened charge density is calculated. The screening potential is calculated by Poisson's equation. The dielectric matrix, then, comes out to be of the following form:

$$\epsilon(q, q') = \delta_{q, q'} - v(q) \chi^0(q, q')$$

where the polarizability tensor $$\chi^0(q, q')$$ is defined as

$$\chi^0(q, q') = \sum_{k, \mu} \sum_{k', \mu'} f^\mu_{k', \mu} - f^\mu_{k, \mu} - \frac{E_{k, \mu}}{E_{k', \mu}} \left< \phi_{k, \mu}^0 \left| \exp(iq \cdot r) \right| \phi_{k', \mu}^0 \right> \times$$

$$\times \left< \phi_{k, \mu} \left| \exp(iq' \cdot r) \right| \phi_{k', \mu} \right>$$

Here $$k, \mu$$ is the band index and $$v(q)$$ is equal to $$\frac{\alpha e^2}{|q|^2}$$.

For a crystalline solid the above expressions can be written in terms of wave vector $$\vec{q}$$ restricted to the first Brillouin zone:

$$\epsilon(q + \vec{G}, q + \vec{G'}) = \delta_{q + \vec{G}, q + \vec{G'}} - v(q + \vec{G}) \chi^0(q + \vec{G}, q + \vec{G'})$$

where,

$$\chi^0(q + \vec{G}, q + \vec{G'}) = \sum_{k, \mu} \sum_{k', \mu'} \left[ f^\mu_{k', \mu} - f^\mu_{k, \mu} - \frac{E_{k, \mu}}{E_{k', \mu}} \right] \left< \phi_{k, \mu}^0 \left| \exp(iq + \vec{G} \cdot r) \right| \phi_{k', \mu}^0 \right> \times$$

$$\times \left< \phi_{k'} \left| \exp(-i(q + \vec{G}) \cdot r) \right| \phi_{k', \mu} \right>$$

Here, $$k = k' + q + \vec{H}$$ and $$\vec{H} = \vec{G} + \vec{G'}$$ is reciprocal lattice vector. Note that $$\vec{G}$$ is also reciprocal lattice vector. The above description is based on Hartree approximation. 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 in the calculation of $$\epsilon(W)$$ [Nozieres and Pines (1958a, 1958b, 1959)].

To account for these effects the effective electron-electron interaction in the Fourier space is written as

$$v^*(q) = v(q) [1 - f_{xc}(q)]$$

(2.108)
The function $f_{xc}$ accounts for the exchange and correlation interactions. The exchange and correlation interactions have been investigated extensively for the free electron as using many body perturbation theory [Geldart and Vosko (1966), Geldart and Taylor (1970), Toigo and Woodruff (1970), Singwi et al. (1970), Vashishta and Singwi (1972), Lindgren and Schwarz (1972), Animalu (1965), Hubbard (1957, 1958), Sham (1961), Ichimaru and Ustumi (1981a,b,c), Sarkar et al. (1999)]. The relevant expressions for $f_{xc}$ are given elsewhere in the present thesis. The basic problems in the dielectric matrix approach to study lattice dynamics of $d$-band metals are the following:

1. How to account for the electronic band structure in the calculation of $\epsilon (\mathbf{q} + \mathbf{G}, \mathbf{q} + \mathbf{G}')$, and

2. How to invert this infinite dimensional dielectric matrix?

These questions have been attempted by several authors [Ferreira and Parrola (1971), Hanke and Bilz (1972), Hanke (1973), Sham (1971), Pick (1971), Sinha (1968), Prakash and Joshi (1970, 1971), Singh and Prakash (1977)].

Wang and Overhauser [(1987a,b, 1988)] have proposed a dynamic pseudopotential model. In this model, in fact, the pseudo charge density $\rho (\mathbf{r})$ is modelled

$$\tilde{\rho} (\mathbf{r}) = \rho_c (\mathbf{r}) + \rho_s (\mathbf{r})$$

where $\rho_c (\mathbf{r})$ arises from the inner ion core and $\rho_s (\mathbf{r})$ from the outermost filled electron shell. Thus, pseudopotential of each ion has two parts: one for the core and one for the shell. The conduction electrons screen all 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. The dynamical matrix, in this theory, has the form

\[
\begin{bmatrix}
D_{cc} & D_{cs} \\
D_{sc} & D_{ss}
\end{bmatrix}
\begin{bmatrix}
A\hat{\alpha} \\
B\hat{\beta}
\end{bmatrix}
= 
\begin{bmatrix}
nM\omega^2 A\hat{\alpha} \\
nm\omega^2 B\hat{\beta}
\end{bmatrix}
\] (2.110)

Here each matrix \(D\) is 3x3 matrix. \(n\) is atomic density. \(\hat{\alpha}\) and \(\hat{\beta}\) are unit polarization vectors for core and shell respectively. \(A\) and \(B\) are corresponding amplitude. \(Z\) is number of shell electrons. \(m\) is the mass of electron.

\[
\begin{align*}
D_{\gamma\gamma}(cc) &= 4\pi n^2 \left[ \sum_\mathcal{G} \frac{|\rho_c(\mathcal{G} + \mathcal{q})|^2 (\mathcal{G} + \mathcal{q})_i (\mathcal{G} + \mathcal{q})_j}{|\mathcal{G} + \mathcal{q}|^2 \varepsilon_{cc}(\mathcal{G} + \mathcal{q})} ight] \\
&\quad - \sum_\mathcal{G} \left[ \frac{|\rho_c(\mathcal{G})|^2}{\varepsilon_{cc}(\mathcal{G})} + \frac{\rho_s(\mathcal{G})}{\varepsilon_{ss}(\mathcal{G})} \right] \frac{\mathcal{G}_i \mathcal{G}_j}{\mathcal{G}^2} \right] \\
D_{\gamma\gamma}(cs) &= 4\pi n^2 \sum_\mathcal{G} \rho_c(\mathcal{G} + \mathcal{q}) \rho_s(\mathcal{G} + \mathcal{q}) \frac{\mathcal{G} + \mathcal{q}}{(|\mathcal{G} + \mathcal{q}|^2 \varepsilon_{ss}(\mathcal{G} + \mathcal{q}))} \frac{\mathcal{G} + \mathcal{q}}{(|\mathcal{G} + \mathcal{q}|^2 \varepsilon_{cs}(\mathcal{G} + \mathcal{q}))} \frac{\mathcal{G} + \mathcal{q}}{(|\mathcal{G} + \mathcal{q}|^2 \varepsilon_{cc}(\mathcal{G} + \mathcal{q}))} \] (2.111)
\]

An interesting point in this formalism is to model the pseudo-ion core and shell, change densities \(\rho_c(\mathcal{r})\) and \(\rho_s(\mathcal{r})\). Each worker will naturally have his own preference in such matter. This model was applied to compute phonon dispersion of 12 metals including \(Cu, Ag, Au, Ca, Sr, Ba\) and \(Yb\) with reasonably good success. The model was also used to study phonon spectra of liquid an amorphous metals.

### 2.2 Historical Survey

Different forms of pseudopotentials suggested for transition metals are given in Table 2.1. In the same table, we also mention their applications upto 1988. In the following, we outline the applications of various approaches from 1988 onwards.

The Embedded Atom Model (EAM) has been applied to calculate the phonon
frequencies of transition metals $Ni$, $Pd$ and $Cu$ by Ningsheng et al. [1989]. It was found that EAM with the first neighbour potential cannot assure to reproduce the phonon frequencies at zone boundary. 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 inter-ionic potentials obtained in the second order relative to the electron-ion interaction pseudopotential $V_{ion}$ to the modelling of lattice defects in transition metals. Appropriate adjustable $v_{ion}$’s are proposed. Yokayama et al. [1989] have suggested a method of extracting anharmonic inter-atomic potential from extended X-ray absorption fine structure. Straub et al. [1988] have studied the elastic moduli of $Cu$ under compression at 0°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.

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. Cohesive energies, bulk moduli and equilibrium lattice constants were calculated for 4$d$ and 5$d$ 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.
Table 2.1
Different Forms of Pseudopotentials for Transition Metals

1. Borch and De Gennaro [1970a,b]

\[ v_{\text{pon}}(r) = \begin{cases} \frac{V_0}{r} & \text{for } 0 < r < r_1 \\ -A & \text{for } r_1 < r < r_2 \\ -\frac{2\varepsilon^2}{r} & \text{for } r_2 < r \end{cases} \]

In \( q \)-space,

\[ v(q) = -\frac{4\pi \varepsilon^2}{\Omega_{\text{eq}} r} \left\{ \cos(qr_2) + \frac{1}{q} \left[ \sin(qr_2) - \sin(qr_1) \right] - (qr_2) \cos(qr_2) + (qr_1) \cos(qr_1) \right\} \]

The authors have used potential to calculate the electronic contribution to the low temperature thermal conductivity of noble metals [Idress et al. (1981)] presented an analysis of the model potentials proposed for noble metals [Borch and DeGennaro (1970), Anmalu (1973), Kulshrestha et al. (1975), Sharma (1978)]. It was concluded that pseudopotential of Borch and DeGennaro is the only one giving some overall agreement with the experiments when band gaps, liquid metal resistivities and thermo-electric power are calculated.

2. Nand et al. [1975, 1976a,b]

In \( r \)-space

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

In \( q \)-space,

\[ v_{\text{pon}}(q) = -\frac{4\pi \varepsilon^2}{\Omega_{\text{eq}} r^2} \left[ \sin qr_2 - \frac{4r_2}{r_2-r_1} \right] \frac{q^2 r_2^2 \sin qr_2}{(1+q^2 r_2^2)^{3/2}} \exp \left( \frac{r_1}{r_2} \right) \]

\[ -\frac{r_2}{r_2-r_1} \frac{qr_2 \exp \left( \frac{r_1}{r_2} \right)}{\exp \left( \frac{1}{1+q^2 r_2^2} \right)^{3/2}} \left\{ 8qr_2 \cos qr_2 + \sin qr_2 \left( 3 - 6q^2 r_2^2 - q^4 r_2^4 \right) \right\} \]

The pseudopotential is used to study thermal properties, phonon dispersion, binding energy and compressibility of the noble metals. Gupta et al. [1986] have used this model potential to compute phonon spectra of \( Ba \).


In \( q \)-space

\[ v_{\text{pon}}(q) = \frac{1}{\Omega_{\text{eq}}} \left[ -\frac{4\pi \varepsilon^2}{q^2} + \beta \exp \left( -q^2 R_0^2 \right) \right] \]

This model was used to study phonon dispersion in noble metals [George et al. (1978), Gohel et al. (1985)].
4. Kumar and Hemkar [1978]

Authors calculate phonon dispersion curves of Au.

\[
V_{\text{ion}}(r) = \begin{cases} 
\frac{2e^2 r_s}{r_{c+d}(r_{c+d}-r_s)}, & r < r_s \\
-\frac{2e^2}{r_{c+d}}, & r_s < r < r_{c+d} \\
-\frac{2e^2}{r}, & r > r_{c+d}
\end{cases}
\]

In q-space,

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

(\cos q r_{ps} - \sin q r_{ps})

5. Vrati et al. [1977, 1979]

Phonon dispersion curves of Ag [Vrati et al. (1979)] and Th [Vrati et al. (1977)], phonon anomalies in Ni, Pd, Pt [Vrati et al. (1980)].

6. Khanna [1981a,b]

The present pseudopotential was used to compute form factors, interatomic potential, liquid metal resistivity and thermo-electric power and binding energy of Ag and Au and dispersion curves of Au.

7. Krasko-Gurskii [1969a,b]

The authors used their own pseudopotential with ionization energy as an input parameter and with HSGW screening for Ca, Sr and Ba [Krasko-Gurskii (1971)]. Kiejna [1980] has tested the validity of this pseudopotential by calculating form factors, liquid metal resistivity for Cu. Prasad et al. [1984] have used \( KG \) potential to compute lattice dynamics of Ca. Rosengren et al. [1975] used present form to study phonon dispersion curves, elastic constants, binding energy, bulk modulus and Debye temperature of Th.
8. Kulshrestha et al. [1975, 1976]

The authors have used the present pseudopotential to calculate phonon dispersion and elastic constants of noble metals. The pressure-volume relations and pressure derivatives of elastic constants for noble metals were studied by Soma et al. [1981] using this model. Soma et al. [1987] have calculated the temperature dependence of the mean square displacement and melting temperature vs. pressure relations for noble metals using the treatment of lattice dynamics on the basis of the present model potentials.


In r-space,

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

In q-space,

\[ v_{\text{ion}}(q) = \left( \frac{4\pi}{\Omega_0 q^3} \right) \left( q^2 (Ar_m - Ze^2) \cos qr_m \right) - (Ar_c \cos qr_c) + q \left( (A - R) \sin qr_c \right. \right. \\
- A \sin qr_m + \left( \frac{2R}{r_c} \right) (1 - \cos qr_c) \right) \]

with \( A = \frac{2Ze^2}{r_m} \)

The pseudopotential is used to study dispersion curves, binding energy, compressibility and elastic constants of Cu and Au.

10. Idress et al. [1982]

In r-space,

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

In q-space,

\[ v_{\text{ion}}(q) = \frac{4\pi}{\Omega_0 q^3} \left( \begin{array}{c} (ARm^2 + B - AR_W R_m) \\ (\sin qr_m - qr_W \cos qr_m) \\ -B (\sin qr_W - qr_W \cos qr_W) \\ -AR_W q \\ +2 (\cos qr_m - 1) - Ze^2 q \cos qr_W \end{array} \right) \]

The present pseudopotential was used to compute liquid metal resistivity, band gaps, thermo-electric power and inter-atomic potential for noble metals.
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 inter-atomic potential. Pressure influence on the lattice properties was studied for small compressions (mode Grüneisen 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 Grüneisen 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. Greenberg et al. [1990] have extensively discussed the possibility of describing lattice properties of Ir in terms of pseudopotential theory. 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. To calculate lattice dynamics of h.c.p. transition metals Sc and Y, Singh [1990a] has considered the ion-ion interaction on the line of Wills and Harrison [1983]. In this work, an exponentially damped pair potential was taken for s-electron contribution. The interaction potential was coupled with a temperature factor of the type \( \exp \left( -\frac{\pi K_T T}{\hbar \omega_q} \right) \) [Tanaka and Yamanoto (1977)]. A real space treatment required the interactions up to 11th neighbour for proper convergence. 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 ab initio plane wave basis. Onwuagba's scheme of incorporating local field correction to the dynamical matrix was extended to molybdenum and tungsten by Okoye and Pal [1990]. 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), \( d - d \) 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 metal by Singh and Singh [1990a,b]. 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. Zoli [1991] has calculated the atomic mean square displacement of Al, Cu, Ag and Au with a force constant model potential. The harmonic and anharmonic contributions have been parametrized. It is shown that the inclusion of the anharmonic effects in the phonon spectra allows results to be obtained that are in good agreement with the experimental data. The first principles generalized pseudopotential-theory of bulk transition metal inter-atomic potentials was extended by Moriarty and Phillips [1991] to surfaces by transforming the total energy functional to a local environment representation in which both the volume terms and the multi-ion potentials were modulated by local averages of the electron
density or the density of states. This theory encompasses and goes beyond simple embedded-atom schemes by including the angular forces necessary to treat the central b.c.c. metals. Applications to the vacancy-formation, and free surface energetics of Cu and Mo were discussed. The isothermal equation of state of a solid at a given temperature can be used to describe the relation between the pressure and compressions [Muraghan (1944), Birch (1952), Vinet et al. (1989, 1986)]. Li Rong Chen and Quing Hu Chen [1991] have discussed these equations of state and have compiled the compressibility data for the 15 transition metals. This paper includes the data of pressure derivative of bulk modulus. Mei et al. [1991] have presented a simple analytic embedded atom model which includes more than nearest neighbours. These authors have calculated parameters for Cu, Ag, Au, Ni, Pd and Pt. The model was applied to study the thermodynamical properties of these metals with molecular dynamics. The calculated fractional density change on melting, heat of fusion, linear coefficient of thermal expansion and heat capacities above room temperature were found in good agreement with experiments. Mishra et al. [1991] have modified Morse potential to include three-body interactions along with two-body interaction. This interaction involving six adjustable parameters was applied to Pb, Pt and Pd to study phonon dispersion curves. Mishra and Rathore [1989, 1990] have also separated two- and three-body parts for compressibility on lines of Mohammad et al. [1983, 1984]. Sears and Shelley [1991] have discussed the importance of variation of Debye-Waller factor and proposed a simple model which is based on the familiar high and low temperature expansions. This model allows one to determine the quantity at an arbitrary temperature with a typical accuracy of 2 to 3%. Bylander and Kleinman [1992] have introduced a new projection operator replacing old one in Phillips-Kleinman 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. Mujibur Rahman and
Salek [1992] have used the inter-atomic interaction constructed from Aschroft empty core model to compute temperature variation of Einstein's temperature and elastic constants. The temperature dependence of these properties is taken into account through changes in the number densities. Eriksson et al. [1992] have computed electronic, quasi-harmonic and anharmonic entropies of transition metals from linear muffin-tin orbital electronic densities of states (using both the atomic-sphere approximation) as well as a full potential. Gareia et al. [1992] have used two gradient-corrected exchange-correlation functionals in the framework of *ab initio* pseudopotential method to compute lattice constant, bulk modulus and cohesive energy of Al, Si, Ge, GeAs, Nb and Pd. Sugiyama [1992] has presented an asymptotic expansion of $V_{\text{ion, pair}}$ at non-zero temperature. The author uses modified Lighthill's method which allows to derive $V_{\text{ion, pair}}(r, T)$ in the usual way that is used in pseudopotential treatment of $V_{\text{ion, pair}}(r, o)$.

Gurica et al. [1992] have used two gradient-correction exchange-correlation functionals in the framework of *ab initio* pseudopotential method to compute lattice constant, bulk modulus and cohesive energy of Al, Si, Ge, GaAs, Nb and Pd. Singh et al. [1992] have applied generalized exponential potential along with Born-Mayer potential to study lattice dynamics of Sc, Zr and Mg. Wolf et al. [1992] have studied the elastic constants of f.c.c. palladium as a function of temperature for four different embedded-atom method models. Kresse et al. [1992] have investigated the construction of norm-conserving "soft core" pseudopotentials with improved convergence properties of the plane waves and perturbation expansions. The total kinetic energy is found to control the convergence. 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 Tc metals. Barrera and Batana [1993b] have obtained general expressions to calculate the first, second and third order coupling parameters considering a general inter-ionic 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 up to third neighbours while 3-body forces up to nearest neighbours are taken. The model uses four independent parameters. The metals studied are Ni, Pd and Pt. To study thermal expansion of f.c.c. metals Barrera and Batana [1993b] have proposed an inter-ionic 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. 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 γ-Fe. The phonon dispersion curves of γ-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. was used to calculate lattice dynamics of α-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. Soderlind et al. [1993] have used a full potential linear muffin-tin orbital method [Wills and Copper (1987) and Wills et al. (1992)] as well as a linear muffin-tin orbital atomic sphere approximation to calculate elastic constants of 3d, 4d and 5d metals. These authors have also demonstrated a simple correlation between $C'$ and the magnitude of the f.c.c.-b.c.c. crystal structure energy difference. 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 inter-atomic force constants using non-local \textit{ab initio} pseudopotentials. Cleri and Rosato [1993] have developed many body potentials based on the second moment approximation of tight binding Hamiltonian. This has been applied to Cu, Ag, Au, Ni, Pd and Pt to compute phonon spectra and elastic constants. 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.
Kraft et al. [1993] have used first principles full potential non-relativistic calculations to obtain total energy of f.c.c. Cu for various deformations. There are presently experimental data on f.c.c. metals concerning both fundamentally harmonic and anharmonic properties. At present there is not a simple inter-ionic 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. Singh and Yadav [1994] have used previously mentioned real space analysis to calculate binding energy and elastic constants of f.c.c. transition metals. Ivanov et al. [1994] have measured and analysed the phonon dispersion curves of Ir. The analysis is based on simple pseudopotential due to Heine and Aberenkov [1964]. This pseudopotential has been used to compute inter-atomic potential for Ir and Rh. These potentials show interesting features: (i) rigidity at small distances, and (ii) weakly pronounced Friedel oscillations. Elastic properties, phonon spectra, the formation energies of vacancies, interstitial atoms and stacking faults as well as the migration energies of vacancies and interstitial atoms in Ir and Rh have been calculated. Shukla [1994] has evaluated quasi-harmonic and anharmonic contribution to atomic mean square displacement or Debye Waller factor of f.c.c. metals. The inter-ionic potential used in this work is the Lennard-Jones potential. Verma et al. [1994] have proposed a generalized form of inter-atomic potential which has an exponential form and which includes two-body and three-body forces. This model was used to study second order and third order elastic constants, cohesive energy and phonon spectra with a reasonably good success. 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. Sigalas and Papaconstantpoulos [1994] have presented a method of fitting augmented plane wave energy bands and total energy results for the f.c.c.
and b.c.c. structures to a simple pair potential that is designed to account for all the terms of total energy except non-orthogonal tight binding Hamiltonian. They applied this method to calculate the elastic constants of Rh, Pd, Ta, Ir and Au. The results were in good agreement with both first principles local density functional theory calculations and experiment. Sugiyama [1994] has extended his work on asymptotic expression for the inter-ionic potential at non-zero temperature. Ahuja et al. [1994] have examined the influence of pseudo-core valence band hybridization on the crystal structure phase stabilities of transition metals under extreme compressions. It was found that for extreme compressions the pseudo-core $p$ states become broad and start to hybridize with the valence states. This results in a modification of the electronic structure and consequently unexpected crystal structures become stabilized. This study was carried out on Y, Tb, Rh, Pd and Pt. It was found that Rh, Pd and Pt become b.c.c. below the compression $V/V_0 = 0.4$. Using multi-ion inter-ionic 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]. Söderlind et al. [1994] have used full potential linear muffin-tin orbital (FP-LMTO) method to calculate the elastic constants for Cr, Fe, Ni and CO. It was found that behaviour of the elastic shear constant $C'$ could be understood from the filling of spin-down $3d$ band for the ferro-magnetic elements. Upadhyaya et al. [1994] have used angular forces of Clerk, Gazis and Wallis type to calculate phonon dispersion in Be, Tb, Ho and Lu. 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. Singh and Yadav [1994] have defined an inter-atomic potential as

$$V(r) = [V_{FE}(r) + V_d(r) + V_{ad}(r) + V_f(r) + V_{ff}(r)] \exp \left( -\frac{\pi K_BT_r}{\hbar \nu_f} \right)$$
where

\[ V_{FE}(r) = \frac{2\pi^2}{r} \left[ H_1 (r - 2r_c) + \frac{1}{4} H_3 (r - 2r_c) + \frac{1}{2} H_2 (r) \right. \]

\[ \left. + \frac{1}{4} H_3 (r + 2r_c) - \frac{1}{4} H_3 (r + 2r_c) \right] \]

where \( H_1, H_2 \) and \( H_3 \) are represented as the sum of the repulsive and the oscillatory contributions. This model was used to compute elastic constants of nine transition metals and four rare earths and actinides. Rose and Shore [1994] have explained the trends in the elastic constants of the simple and transition elemental cubic metals in terms of uniform electron gas theory. It was shown that the elastic constants of the elemental cubic metals depend primarily on the bonding valence, the density at the cell boundary and the symmetry of the lattice. Fang and Chen [1994] have presented a simplified treatment to study the effect of pressure on melting temperature of simple and noble metals. This method is based on Lindemann's law and Debye model and the assumption that the Grüneisen parameter divided by volume is constant. 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 (using empty core model), 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. The following metals were studied: \( Ti, V, Cr, Mn, Fe, CO, Ni \) and \( Zr \). Recently, there has been great interest in non-crystals, witness a review with 396 references [Gleiter (1989)]. In this regard, Kaufman and Schlosser [1995] have prepared a thermodynamic model for solids under pressure by assuming the universal equation of
state and that under zero pressure the free energy is equal to the harmonic crystal (Debye) free energy. The model was applied to gold. In the case of non-crystals this model reproduces the observed enhancement of the isobaric heat capacity and of the thermal expansion. Okjun [1995] has used an $N$-body potential energy function, constructed empirically to study the dynamical behaviour of $C_u$ and $N_s$. 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 Grifalco 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. It is well known that dielectric function of electron gas plays an important role in determining physical properties of metals. Moroni et al. [1995] have calculated the density-density static response of the electron gas at zero temperature and in metallic regime by diffusion Monte Carlo. The computed local field factor $G(q)$ smoothly interpolates between the asymptotic small and large $q$ behaviour with a cross over around $2q_F$. The following simple formula reproduced $G(q)$ at relevant values of the wave vector

$$G(q) = \left( (A - C)^{-n} + \left( \frac{q^2}{Bq_F^2} \right)^n \right)^{1/n} + C \left( \frac{q}{q_F} \right)^2$$

with $n \approx 8$ for $r_s = 2$ and $r_s = 5$ and $n = 4$ for $r_s = 10$. It was found that this equation with $n = 8$, the numerical values of $G(q)$ for different $r_s$ have been given for $q$ up to 4.23 $q_F$ [Moroni et al. (1995)]. 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. Fiolhais et al. [1995] have significantly noticed that the properties of the
simple metals are controlled largely by three density parameters. The equilibrium average valence electron density $\frac{3}{4\pi r_s^3}$, the valence $z$ and the density on the surface of Wigner-Seitz cell, represented by the equilibrium number $N_{int}$ of valence electrons in the interstitial region. These authors proposed a structured local electron-ion pseudopotential $W(r)$ which depends upon either and $z$ ("Universal choice for Nint) or $r_s$, $z$ and Nint for each metal ("Individual" potential). Calculated binding energies, bulk moduli and pressure derivatives of bulk moduli, evaluated in second order perturbation theory are in good agreement with the experiments for 16 simple metals and the bulk moduli are somewhat better than those calculated from first principles non-local norm-conserving pseudopotentials. Isoardi et al. [1995] have proposed a simple model of inter-ionic 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. Guevara et al. [1995] have proposed a semi-empirical model potential to simulate properties of f.c.c. transition metals. The attractive part of the potential has been obtained from a tight binding Hamiltonian that takes into account the symmetry of the $d$-orbitals and leads to $2/3$ power dependence on the effective coordination (or second moment of the local density of states) instead of the usual square root dependence. The repulsive interaction is assumed to be of Born-Mayer type. Four parameters are adjusted with the experimental data. Two different parametrizations have been suggested. The calculations of bulk defect, surface and cluster properties were made. The attractive and repulsive
parts are as follows:

\[ E_R^i = -\xi \left( \sum_j e^{2q \left( \frac{r_j}{r_0} - 1 \right)} \right)^{2/3} \]
\[ E_R^i = A \sum_j e^{-p \left( \frac{r_j}{r_0} - 1 \right)} \]

\( \xi, q, A \) and \( p \) are parameters. \( r_0 \) is the nearest neighbour distance. De Girocoli [1995] has successfully computed phonon dispersion curves of Nb using density functional perturbation theory. Cho and Kang [1995] have studied the ground state properties of \( N \) by using the plane wave basis potential core pseudopotential scheme and the local spin density approximation. The calculated lattice constant, bulk modulus and magnetic moment are in good agreement with the previous all electron LSDA calculations and experiments. It was found that the ground state properties of \( N \) are described well even by the use of very soft d-pseudopotentials. The present results demonstrate well the reliability of the pseudopotential scheme in describing the 3d-transition metals. Lattice dynamical calculations have been performed in real space approach using Rare Earth Metal Model potential for HCP rare earth metals by Singh [1995]. 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. These authors have proposed the following form of pseudopotential

\[ V_{\text{ion}}^{(r)} = \left[ \frac{ae^2}{r_i - r_c} \right] \left[ r_i - r_c \right] - \frac{mze^2}{r_i} e^{-\left( r_i - r_c \right)/r_c} \text{ for } r < r_i \]
\[ = -\frac{mze^2}{r} \text{ for } r > r_i \]

where

\[ m = \exp \left[ \frac{(r_i - r_c)}{r_c} \right] \]

It is obvious that the potential is repulsive from \( r = 0 \) to \( r = r_c \), attractive for \( r > r_c \) and assumes a Coulombic form for \( r > r_i \), where \( r_c \) and \( r_i \) denote core and ionic radii respectively. The repulsive part from \( r = 0 \) to \( r = r_c \) arises due to tightly bound inner core states and the attractive part from
$r = r_c$ to $r = r_s$ is due to $s - d$ hybridization. In the computation of phonon dispersion curves, $r_c$ was kept constant and $r_s$ was varied to reproduce frequency of [111]I branch. The authors computed second order elastic constants also in the long wavelength limit.

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 \textit{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.

Higher order elastic constants is a measure of the anharmonicity of a solid. Sindhu and Menon [1996] have derived the expression for parameters of elastic waves and low temperature thermal expansion of h.c.p. systems. Milstein et al. [1996] have studied general behaviour associated with the branching of cubic crystal at shear modulus instabilities under
a hydrostatic environment. It was noted that stable ranges of the tetragonal structures at very high pressures do exist. Peng et al. [1996] have computed Debye-Waller factors and absorptive scattering factors for 44 elemental crystals from the experimentally determined phonon density of states. Saxena et al. [1996] have used a local model potential for Y, Zr, Nb, Mo, Ru, Rh and Pd to calculate the binding energy. Wojciechowski [1996] has applied the stabilized uniform metallic electron gas model and has used the concept of metallic valence to compute bulk moduli of transition metals. Makino [1996] has proposed that the bulk moduli $B$ of elemental substances can be determined by the effective pseudopotential radius $r_{ps}$ through an empirical relation $B = C r_{ps}^{-m}$ where $C$ and $m$ are constants. For 5$d$ transition metals $d = 6$. Kresse and Furthmüller [1996] have presented a scheme to calculate the Kohn-Sham ground state of metallic systems using pseudopotentials and plane wave basis state. The scheme includes the application to transition metals. Nogueira et al. [1996] have examined the transferability of local pseudopotentials based on solid state density parameters. Employing a high precision band structure method (FP LAPW - full potential linearized augmented plane wave), Sliwko et al. [1996] have calculated the total energy variation along the tetragonal distortion path connecting the b.c.c. and f.c.c. structures for some simple and two transition metals $T_2$ and $V$. Fang [1996] has derived the following expression for volume dependence of melting temperature from Linde mann's law and Debye model.

$$T_m = T_{m_0} \left( \frac{\Omega}{\Omega_0} \right)^{2/3} \exp \left\{ \frac{2\gamma_0}{q} \left[ 1 - \left( \frac{\Omega}{\Omega_0} \right)^q \right] \right\}$$

This expression is based on the assumption that

$$\frac{\gamma}{\gamma_0} = \left( \frac{\Omega}{\Omega_0} \right)^q$$

Here, $T_{m_0}$ is melting temperature at atomic volume $\Omega_0$ and $T_m$ corresponds to atomic volume $\Omega$. $\gamma$ and $\gamma_0$ are Grüniesen parameters at volumes $\Omega$ and $\Omega_0$. 57
respectively. Cho and Scheffler [1996] have studied the ground state properties of $Fe$, $Co$ and $Ni$ with the LAPW method and norm-conserving pseudopotential and magnetic moment with both local spin density approximation and the generalized gradient approximation are in good agreement with those of all-electron calculations respectively. A variant of the Vanderbilt [1996] ultrasoft pseudopotential scheme, where the norm conservation is released for only one or a few angular channels, has been presented by Stokbro [1996]. With this scheme, some difficulties of the truly ultrasoft pseudopotentials are overcome without sacrificing the pseudopotential softness. The density based pseudopotentials (local) [Fiolhais (1995, 1996)] were tested for sixteen simple metals by Pollack et al. [1997] in its ability to reproduce band structure, lattice vibrations and electrical resistivity of liquid metals. 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. 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 $Rh$. A special feature of this work is that it requires an empirical adjustment of pseudopotential form factor in certain region of $q$ space. Karimi et al. [1997] have examined the reliability of embedded atom method in predicting thermal properties of $Ni$. The authors have calculated elastic constants, compressibility, specific heat and coefficient of thermal expansion of $Ni$ as a function of temperature. Anderson [1997] has investigated the conditions under, which the thermal pressure $P_{Th}$ is independent of volume in solids. Kuchhal et al. [1997] have discussed a temperature dependent equation of state of condensed matter which is capable of predicting the high pressure and
high temperature behaviour of solids and liquids. Ostanin and Trubistin [1997] have used FP-LMTO method to calculate the total energy and equilibrium lattice properties for the observed phases of Ti. Sarkar and Sen [1997] have applied the localized version of the density functional based norm-conserving pseudopotential to the study of liquid phonons and surface dynamics. Paidar et al. [1997] have studied elastic constants of f.c.c. transition metals on the basis of a many-body potential based on the second moment approximation of the d-electron density of states. Doyama and Kogure [1997] have suggested a new embedded atom potential for Cu, Ag and Au. Thermal expansion and equation of state of Ir and Rh were studied by Katsnelson et al. [1997]. This study was based on a local model pseudopotential. Ostanin et al. [1997] have used FP-LMTO method to study total energy, equilibrium lattice constant and the bulk modulus of f.c.c. Fe. Kallinteris et al. [1997] have presented an alternate approach to parametrizing the expression for the total energy of solids within the second moment approximation of the tight binding theory. Corso [1997] have generalized the density functional perturbation theory for lattice dynamics to Vanderbilt's ultrasoft pseudopotentials. Yakibchuk [1997] has set an effective inter-ionic interaction for transition metals from third order perturbation expansion of non-local pseudopotentials. Kavner and Jeanloz [1998] have measured the variation of melting temperature with pressure for Pt up to 70 GPa. Fang [1998] has derived a universal relation, from the diffusion-vibration theory and a thermodynamic identity, for pressure dependence of melting temperature. However, this relation has not been yet tested for different groups of metals except alkali metals Li, Na, K. Sarkar et al. [1998] have proposed a simple parametric form for the static local field factor $G(q)$ which appears in the dielectric function $\epsilon(q)$ improved for exchange and correlation effects

$$G(q) = A \left\{ 1 - \left[ 1 + B \left( \frac{q}{k_f} \right)^4 \right] exp \left[ -C \left( \frac{q}{k_f} \right)^2 \right] \right\}$$
where \( A \) and \( C \) determine the two limiting behaviour of \( G(q) \) and \( B \) is given by

\[
B(r_s) = a + br_s + Cr_s \sum_{n_r} + \frac{d \sum_{n_r} e^r}{r_s^2} + \frac{e}{r_s^2}
\]

with \( a = 0.0301412 \), \( b = -0.0084724176 \), \( c = 0.0016291083 \), \( d = -0.2386599 \), and \( e = 0.27960609 \).

Eichler et al. [1998] have calculated phonon dispersion relation in f.c.c. \( Rh \) by using *ab initio* local density functional (LDF) calculations and inelastic neutron scattering measurements. The LDF calculations have been performed both using ultrasoft pseudopotentials and a plane wave basis and norm-conserving pseudopotentials and a mixed basis set. By using the so-called "universal" cold equation of state of solids (EOS) proposed by Vinet et al. [1987] and a Debye-Grüneisen expression for the thermal pressure, an EOS for extended P-V-T condition has been proposed by Fernandez [1998]. Shrivastava et al. [1998] have numerically evaluated the structure factors \( S(q) \) for transition metals at low temperatures. These authors have used Krebs' phenomenological model [1965] of lattice dynamics. The calculations were made for \( Fe \), \( W \) and \( V \). The method presented here could be used to compute \( S(q) \) for large number of elements where the measured phonon spectra can be used. We wish to consider this problem in future. Heid et al. [1998] have investigated the phonon dispersion spectrum of \( Ir \) within the framework of first principles pseudopotential mixed basis method. Remarkable irregularities in the behaviour of the binding energy versus distance function of solids were reported by Rose et al. [1981, 1983]. Garces and Guillermé [1998] have considered this approach to correlate and predict cohesive properties and parameters of equation of state for solids. Osetsky [1998] has used a pair potential model describing inter-atomic interactions in \( \gamma \) and \( \delta \) iron based on generalized pseudopotential theory. The model has been shown to be fairly reliable. Bauer et al.
[1998] employed a linear response approach based on density functional theory to compute phonon dispersion curves of Al, Au, Na and Nb. These authors also studied the electron-phonon interaction and hence temperature variation of electrical and thermal resistivities. Pohlong and Ram [1998] have constructed the embedded atom method potentials for Cu, Ag, Au, Ni, Pd and Pt. The lattice dynamical results for Cu, Ag and Au were in good agreement with the experiment, but results for Pd, Pt and Ni were not so good. Pollack and Perdew [1998] have studied the effect of local field or exchange correlation corrections on lattice dynamics of several simple metals by using a density based local pseudopotential. Stacey [1999] has proposed a relation connecting $\frac{dK}{dP}$ as a function of $\frac{P}{K}$ where $P$ is pressure and $K$ is bulk modulus. Here, the pressures of geological interest are considered. Singh [1999] has carried out a study of structural energy, phonon dispersion curves and elastic constants of Rh and Ir using the transition metal pair potential. Singh [1999] has also carried out the study of phase transition, cohesive energy, binding energy, bulk modulus and phonon spectra of Cu, Pd and Au using transition metal pair potential. Considering the pressure as an important thermodynamical variable, the efforts to study equation of state both experimentally and theoretically are being made by Godwal and his coworkers [1999]. The dispersion in the entire Brillouin zone and temperature dependence of the anharmonic frequency shift and phonon damping in a number of f.c.c. metals has been investigated by Katsnelson et al. [1999] on the basis of pseudopotential theory for K, Ir, Ca and Sr. Heid and Bohnen [1999] have presented a generalization of density functional based linear response calculations of lattice dynamical properties. The accuracy of the scheme was demonstrated through the calculations of phonon dispersion curves of Ag and Y. Nie and Chen [1999] have compared some equations of state with experimental data. It was found that Birch equation of state is the best. Haas et al. [1999] have studied phonon dispersion curves of Mo at zero temperature as well as at
elevated temperatures using a semi-empirical light binding model. Tewari et al. [1999] have given a technique to obtain differential and total phonon frequency distribution functions from the measured temperature dependent mean square displacements. Jeong and Chang [1999] have performed molecular dynamics simulations to study the shock melting of transition metals Cu, Pd and Pt. A simple analytical two-body potential

\[ \phi(r) = -Ar^{-n} + B\exp\left(-pr^m\right) \]

for simple and transition metals was considered by Kuchhal and Dass [1999]. This interaction potential was used, with Born stability criteria, to compute \( P - V \) relations and third order elastic constants of La, Na, K, Rb, Ta, V, W, Mo and Cr. Ali [1999] has proposed a many-body interaction potential. In this work, the free parameters are determined by using global optimization to perform least square fit to a large number of crystal properties. Zahid et al. [1999] have used a local model pseudopotential of Bretonnet and Silbert [1992] to compute dynamic properties of less simple liquids. Cagin et al. [1999] have studied the temperature dependence of thermodynamic and mechanical properties of Ni, Cu, Ag, Au, Pt and Rh. These authors have used a many body potential due to Sutton and co-workers [1990] in molecular dynamics. Meenakshi and Sharma [1999] have made a test of universality of equations of state by applying them to calculate \( P - V \) relations, isothermal bulk modulus \( K_T \) and pressure derivative of \( K_{T_2} \) in case of different types of solids. Xie et al. [1999] have studied thermal properties of Ag within the quasi-harmonic approximation by using phonon dispersion from density functional perturbation theory and the pseudopotential plane wave method. A number of methods have been used in the literature for Brillouin zone integrations, for example, the Gaussian broadening method, the linear interpolative tetrahedron method, quadratic interpolative tetrahedron method and linear extrapolative method. Pickard and Payne [1999] have presented a highly
efficient extrapolative Brillouin zone integration scheme. Using first principles local density electronic structure calculations Novikov et al. [1999] have investigated the evolution of Fermi surface of h.c.p. \( \text{Zn} \) and \( \text{Cd} \) under pressure. A sequence of electronic topological transitions were found which apparently leads to the experimentally observed anomalies in their lattice parameters. The role of localized bands in the dynamical response of \( \text{Cu} \) has been investigated by Campillo et al. [1999], on the basis of \textit{ab initio} pseudopotential calculations. The equation of state and pressure dependence of elastic constants of \( \text{Mo} \) have been investigated to 24 GPa, experimentally, by Duffy et al. [1999]. Elastic constants of f.c.c. \( \text{CO} \) have been experimentally determined by Gump et al. [1999]. The properties of simple metals are fixed primarily by the equilibrium average valence-electron density parameter \( r_s \) and secondary by the valence \( z \). The simplest level of theory that can account quantitatively for these trends invokes a universal local electron-ion pseudopotential, defined for each pair \((r_s, z)\) and treated as a second order perturbation. Nogueira et al. [1999] have constructed such pseudopotential from two conditions: (1) the total energy should minimize at equilibrium Wigner-Seitz radius \( z^{1/3} r_s \), (2) the bulk modulus should equal the realistic \( r_s \)-dependent prediction of the stabilized jellium model with effective valence \( z^* \). A formal relationship between ultrasoft Vanderbilt-type pseudopotentials and Bl"{u}chl's projector augmented wave method has been derived by Kresse and Toubert [1999]. Dimitrov et al. [1999] have studied both theoretically and experimentally the pair density function of \( \text{Ni} \). By computing the phonon dispersions of a few solids within density functional perturbation theory, Favor and Corso [1999] have compared the performance of the local density approximation with the generalized gradient approximation. Using a many-body potential and molecular dynamics, Pinsook and Ackland [1999] have investigated anomalous phonons and h.c.p.-b.c.c. phase transition in \( \text{Zr} \). The pressure-volume relations in \( \text{Ta} \) have been measured by Cynn and
Yoo [1999] up to 174 GPa. Full potential KKR calculations for total energy of Al, Fe, Ni, Cu, Rh, Ag and Pd have been presented by Asato et al. [1999]. Neumann et al. [1999] have computed elastic constant tensors as function of pressure, for h.c.p. phases of three transition metals Co, Re and Fe using the linearized augmented plane wave method with both local density and generalized gradient approximations. Rumer and Rappe [1999] have designed a non-local pseudopotential with improved transferability. Aschroft’s model potential study of lattice dynamics of α-iron and Barium was carried out by Boselli and Shukla [1999]. Yifang [1999] has extended the analytical embedded atom potentials for f.c.c. and b.c.c. metals to h.c.p. metals. Sirota et al. [2000] have carried out successful calculations of phonon spectra and specific heat $C_V \rightarrow T$ relations for V, Cr, Mn, Fe, CO, Ni and Cu on the basis of Mie-Grüneisen potential

$$\phi(r) = -\frac{a}{r^m} + \frac{b}{r^n}$$

Burakovsky and Preston [2000] have used statistical mechanics of linear defects to obtain a new relation between melting temperature, crystal structure, atomic volume and shear modulus which is accurate to 17% for at least half of the periodic table. The thermodynamic, electronic and magnetic properties of Ni at high pressures have been calculated by Xie et al. [2000] using the ab initio pseudopotential plane wave method and the density functional theory. In the framework of melting as a dislocation-mediated phase transition, Burakovsky et al. [2000] have derived an equation for the pressure dependence of the melting temperatures of the elements valid up to pressures of order their ambient bulk moduli. Soderlind et al. [2000] have calculated monovacancies for seven b.c.c. transition metals V, Cr, Fe, Nb, Mo, Ta and W. A full potential linear muffin-tin-orbital method was used in conjunction with both the local density approximation and generalized gradient approximation. Heid et al. [2000] have investigated lattice dynamics of the transition metal ruthenium both
by inelastic neutron-scattering experiments and by first principles density-functional perturbation calculations. Batani et al. [2000] have reported experimental data on the equation of state of gold in the pressure range 2-10 TPa. Shepard et al. [2000] have reported experimental values of Debye-Waller factors as a function of temperature for Cu, Ag and Pb. Belonoshko et al. [2000] have investigated the melting of Cu by means of molecular dynamic method employing embedded atom type model potential due to Sutton and Chen. Hung and Jindo [2000] have used moment method in statistical dynamics to study the thermodynamic properties of metals taking into account the anharmonicity effects of the lattice vibrations and hydrostatic pressure. The authors have derived the explicit expressions of the lattice constants, thermal expansion coefficient and the specific heats $C_p$ and $C_v$, for cubic f.c.c. metals, within the fourth order moment approximation. The thermodynamic quantities of Al, Au, Ag, Cu and Pt metals are calculated as a function of pressure and they are in good agreement with the corresponding experimental results. The effective pair potentials work well for the calculations of transition and noble metals, compared to the $sp$-valence metals. Dal et al. [2000] have presented the $ab\ initio$ phonon dispersions of magnetic b.c.c. Fe and f.c.c. Ni. The calculations have been carried out in the framework of density functional perturbation theory, using ultrasoft pseudopotentials, spin polarized gradient approximations and nonlinear core corrections. Burakovsky et al. [2000] have derived simple expressions for the melting temperature and latent heat of fusion that depend on the dislocation density at melt. In this theory, melting corresponds to the situation where, on an average, half of the atoms are within a dislocation core. Gornostyrev et al. [2000] have investigated unusual mechanical properties of Ir on the basis of $ab\ initio$ energy local density calculations. Porezag et al. [2000] have investigated the accuracy of pseudopotential density-functional calculations with respect to the corresponding all-electron results. Ostanin et al. [2000] have calculated the
effective potentials for the $E_{eq}$ phonon at the $\Gamma$ point of the Brillouin zone of h.c.p. Zr and the transverse $N$-phonon of b.c.c. Zr, using frozen phonon method, at different pressures. Song et al. [2000] have studied the theoretical tensile strength and bulk modulus of some h.c.p. metals from their electronic structure and binding energy calculations using first principles local density approximation. Systematic \textit{ab initio} calculations of lattice constants, elastic constants and magnetic moments of Fe, CO and Ni in b.c.c., f.c.c. and h.c.p. phases were carried out by Gao and Wang [2000] using \textit{ab initio} local spin-density functional theory. Okube and Yoshiasa [2001] have determined temperature dependence of Debye-Waller factors and anharmonic effective pair potentials for group VII and 1b f.c.c. metals by a cumulant expansion method. Sarkar et al. [2001] have proposed a simple form of the static local field factor which appears in the dielectric screening theory for the most general case of unpolarized interacting electron gas. Sen et al. [2001] have obtained an expression for additional pair potential arising from third order term of pseudopotential perturbation expansion. 300K equation of state, Hugoniot equation of state and Hugoniot temperature for Th and U were theoretically obtained by Li and Wang [2001] using the first principles electronic structure calculations. Cohen and Gulseren [2001] have investigated the thermal equation of state of b.c.c. tantalum from the first principles using the full-potential linearized augmented plane wave and mixed basis pseudopotential method. Aire et al. [2001] have computed the free energy and other thermodynamic properties of hexagonal-close-packed iron by direct \textit{ab initio} methods over a wide range of pressures and temperatures relevant to the Earth's core.

From the historical account of the activities in the field of studying lattice mechanical properties of transition metals given above, the following facts emerge:
1. Most of the investigations in the last decade are based on a density functional theory. However, these investigations differ in respect of the treatment of tightly bound core electrons and/or in the basis set used for describing the wave functions. Also, both local density and generalized gradient approximations are used. Since very accurate full potential calculations (e.g. full-potential linearized augmented-plane wave (FLAPW) calculations) are very time-consuming, even with modern workstations, most studies have been restricted to selected phonon modes by using the frozen phonon approach [Kune (1985)]. Calculations of the entire phonon spectrum have been carried out mostly by using generalized response theory [Baroni et al. (1987), King and Needs (1990)]. Many groups have used the formalism within a plane wave basis and with pseudopotentials [Giannozzi et al. (1991), Pavone et al. (1993), Bungaro et al. (1996) and many other groups mentioned in the historical account]. Linearized-muffin tin-orbitals (LMTO) versions have also been used [Savrasov (1992), Savrasov et al. (1994) and others].

2. A number of attempts have also been made to investigate the lattice properties of transition metals in a relatively simplified way. Such attempts can be classified roughly as follows:

(a) Embedded atom method is semi-empirical in the sense that it requires several experimental inputs. The advantage of this method is that it accounts, through charge densities of neighbouring atoms, for many-body forces.

(b) Purely empirical pair potentials and many-body potentials have also been in use. Purely empirical potentials have no theoretical base. The potentials based on second moment approximation in tight binding method have also been developed.

(c) Generalized pseudopotential theory as developed by Harrison [1969]
and used extensively by Moriarty [1972] has been very useful in predicting the properties of transition metals. \textit{Ab initio} pseudopotentials have also been developed from \textit{ab initio} atomic calculations. Theoretically, they are better than those non-local pseudopotentials which were based on atomic spectroscopic data and quantum defect method.

(d) A widely used approach based on a concept of quasi-localized $d$-states on the background of a nearly uniform electron gas leads to different shell models. These models discussed by Sinha [1980] usually contain free parameters determined by fitting to experimental phonon spectrum. Thus, such an approach is insufficient in predicting the lattice dynamics and is not applicable in studies of static lattice properties.

3. Local pseudopotentials have also been considered. Even transition elements may be described by a local pseudopotential, provided that the valence is chosen appropriately [Starkloff and Joannopoulos (1977), Vanderbilt and Joannopoulos (1983)]. It has been shown that the second order perturbation theory with a local model potential gives a reasonable description of many lattice properties in the case of f.c.c. transition metals [Antonov et al. (1990a), (1990b)].

Recently, Eichler et al. [1998] have shown that pseudopotential techniques may now be used to predict the lattice dynamics of transition metals. These authors have found that different types of pseudopotentials could do the job. Almost a complete account of work based on local pseudopotentials for transition metals is given below: Nearly more than half a dozen local model potentials have been constructed by considering different forms of potentials to represent, phenomenologically, the $s-\text{d}$ hybridization, in real space. Some people have used square well while some have used triangular forms. In few cases, some relatively complicated forms have also
been proposed. Although these authors consider Harrison's generalized pseudopotential theory as the base, nobody has attempted to extract the form, in $q$-space, directly available from this theory. Looking to the fact that even simple model potentials have been fairly successful in reproducing lattice properties of transition metals and fairly simple inter-atomic potentials also do a good job [Antonov (1990a,b), Osetsky (1998), Singh (1999a,b), Katsnelson et al. (1997, 1999), Jeons and Chang (1999), Kuchhal and Dass (1999), Bosseli and Shukla (1999), Hung and Jindo (2000), Sen et al. (2001), Sirotta et al. (2000), Bosseli and Gupta (1993), Mishra et al. (1993), Osman and Mujibur Rehman (1995), Coelho (1996), Raju et al. (1996), Saxena et al. (1995a,b)].

In the light of the above mentioned facts, in the present work, we thought it worthwhile to study a model potential which has been extracted, directly in $q$-space, from Harrison's generalized pseudopotential theory. All these work mentioned here led us to believe that a properly constructed local model potential might lead to reasonably successful results. One such model potential has been constructed in our group. This model potential was first applied successfully by Vyas [2000] and by Pandya [2000] to compute lattice dynamical properties of completely filled and completely empty $d$-band metals respectively. In the present study, we extend the application of this model to partly filled $d$-band metals: Ni, Pd, Pt, Ir, Rh, Fe and Co with a view to see as to how far this model is useful to f.c.c. transition metal group.

As noted above, Antonov et al. [1990a,b] could reproduce many lattice mechanical properties of f.c.c. transition metals with reasonably good agreement with experiments. However, these authors have not considered
the properties like melting temperature as a function of volume, isothermal bulk modulus as a function of temperature, Debye-Waller factor and mean square displacement as function of temperature, and variation of Grüneisen parameter with volume, thermal pressure and thermal expansion. In the present thesis, we, for the sake of completeness and also for better assessment of the model, extend this model to compute the above-mentioned properties. We also complete this study for the metals which were not attempted by Antonov et al.

Although Wills-Harrison's [1983] effective Hamiltonian is useful for several solid state applications, its use in liquid state calculation comes out to be a failure [Regnaut (1989)]. Regnaut's findings have been confirmed by Hausteitner et al. [1991], who have shown that accurate thermodynamically self-consistent integral equation theories of liquids also fail to yield $S(q)$ (structure factor) for $3d$ transition metals with half filled and less than half filled $d$-bands. In the same work Hausleitner et al. [1991] reported that molecular dynamic simulations, using a modified $WH$ potential fail to reproduce reasonable results for the structure of liquids $Ti$ and $V$. These authors conclude that the root of the problem can be traced to the position and depth of the first minimum of the $WH$ potential, and suggest that a successful description of the liquid structure of transition metals require a shallower potential well shifted towards larger values of $r_2$ than those predicted by $WH$. It is to be noted that first principles potentials developed by Moriarty [1988, 1990] which have been successful for solid state properties, are even deeper [Ostetsky (1988), Singh (1999a,b), Katsnelson et al. (1997), (1999), Jeong and Chang (1999), Kuchhal and Dass (1999)]. It is interesting to note that recently Bretonnet and Silbert [1992] have proposed a new model potential for transition metals to obtain effective inter-ionic pair potential. Unlike other model potentials, this potential is based
on observation of Swan [1967] that an approximate potential may be obtained - with reasonable accuracy - from the knowledge of the $d$-phase shift by just using the first two terms of a Dirichlet series sum of short range exponential functions. This model has been found to be extremely useful to compute structural and thermodynamical properties of liquid transition metals [Jakse and Bretonnet (1995), Bhuiyan et al. (1992), Bhuiyan et al. (1993), Zahid et al. (1999)]. However, no attempt has yet been reported at examining the applicability of this model to solid state properties of transition metals. Therefore, in the present thesis, we examine the applicability of this model to solid state properties of transition metals for the first time.

Although there are a large number of papers by different authors with different forms of model potentials, no attempt has been made, quite surprisingly, to carry out a comprehensive study of a large number of lattice mechanical properties in a unified manner. Therefore, in the present thesis, we explore the possibility of successfully calculating a large number of lattice properties at a time.

Transferability and universality in a model potential is highly desirable [Nogueira et al. (1999)]. In order to make a pseudopotential more appropriate from this point of view, we must determine it from some basic parameters, for example, $r_s$, of the metals. The pseudopotential must satisfy the zero pressure (equilibrium) condition also. We have considered these points in the present work. It should be noted that the authors who worked with the local model potentials have not considered these points.

For transition metals, local field effects arising from $s-d$ hybridization are important [Onwuagba (1987)]. Also, many-body effects play an important role [Vyas et al. (2001)]. It has been shown recently by Sen et al. [2001]
that the pair interaction part appearing in the third order perturbation expansion does play an important role in determining physical properties of metals. In the present study, we have incorporated both these effects by a Born-Mayer type term with our model potential as has been done by Antonov et al. [1990a,b]. It is interesting to note that the model due to Bretonnet and Silbert [1992] does not require such a supplement.

In the following, we discuss the construction of model potentials studied presently.

2.3 Pseudopotential Models

1. Model of Antonov et al. [1990a,b]

The description of model starts with an assumption that electron density in transition metal is superposition of nearly free \( s \)-like electrons and quasi-localized \( d \)-like electrons. In several previous works also the same assumption was made [Singh et al. (1988), Sinha (1980), Animalu (1973), Kulshrestha and Upadhyaya (1976), Prakash and Upadhyaya (1988), Vrati et al. (1980), Tripathi and Nand (1979), Kulshrestha and Upadhyaya (1977)]. Thus, we write the total energy at zero temperature as

\[
E = E_t + E_s + (E_{s-d} + E_d + E_{ol})
\]

(2.113)

where \( E_t \) is the energy of electrostatic interaction of ion cores, \( E_s \) and \( E_d \) are the energies of the interaction of the \( s \) and \( d \)-electrons with cores \( s - s \) and \( d - d \) interaction respectively. \( E_{s-d} \) is the hybridization term. \( E_{ol} \) is the energy due to overlap of \( d \)-states at different atomic sites. Antonov et al. represented \( E_s \) term in a form similar to that
obtained for simple metals [Brovman and Kagan (1974), Abarenkov and Heine (1965), Animalu and Heine (1965)]. In the perturbation expansion in simple pseudopotential, $E_s$ can be written as

$$E_s = \sum_{n=0}^{2} E_s^{(n)} + \sum_{n \geq 3} E_s^{(n)}$$  \hspace{1cm} (2.114)

Writing,

$$\phi_d = E_d + E_{sd} + E_{01}$$  \hspace{1cm} (2.115)

Eq. (2.113) can be written as,

$$E = E_t + \sum_{n=0}^{2} E_s^{(n)} + \sum_{n \geq 3} E_s^{(n)} + \phi_d$$  \hspace{1cm} (2.116)

It is clear that $E_t + \sum_{n=0}^{2} E_s^{(n)}$ leads to pairwise interactions. It also contains the volume dependent contribution through $E_s^{(0)}$ and $E_s^{(1)}$.

Now, *ab initio* analysis [Moriarty (1985)] shows that for the closed packed structure (e.g., f.c.c. and h.c.p.) total energy may be represented, with sufficient accuracy, as the sum of volume dependent term and lattice sum of effective pair interaction. This means that

$$\phi_{sr} = \phi_d + \sum_{n \geq 3} E_s^{(n)}$$  \hspace{1cm} (2.117)

must not contain many-body inter-atomic interactions in the case of f.c.c. metals, likely due to cancellation of the many-body contributions of different terms in $\phi_{sr}$. Therefore, we assume that $\phi_{sr}$ contains determinantly, the two-body radial $d-d$ interaction given by repulsive Born-Mayer potential.

$$\phi_{sr} = \frac{1}{2} A \sum_{R} \exp (\alpha R)$$  \hspace{1cm} (2.118)

This analytical form is rather simple and it is valid for interaction of overlapping atomic wave functions [Benedek (1977)]. Thus, the final form of the total energy $E$ is

$$E = E_t + E_s^{(0)} + E_s^{(1)} + E_s^{(2)} + \phi_{sr}$$  \hspace{1cm} (2.119)
where contribution of $s$-like electrons is calculated to second order perturbation theory discussed in the next chapter. The model potential used by Antonov et al. is

$$v_{\text{ion}}(q) = \frac{-8\pi z}{\Omega_0 q^2} \left[(1 + u) \cos qR_0 - U\frac{\sin qR_0}{qR_0}\right] \exp \left(-0.03 \left(\frac{q}{2k_f}\right)^4\right)$$  \hspace{1cm} (2.120)

2. Model of Pandya et al. [2001]

As has been noted earlier, the theoretical workers have used different forms of local model potentials for $d$-band metals. In such work, an effort is made to include some features of Harrison's approach. These various potentials possess, in common, $r$-space phenomenological considerations to account for mainly $s-d$ hybridization. In the present work, we construct a model potential from Eq. (2.15).

Unlike Antonov et al. [1990a], we consider $d$-electron terms also to construct the model. Assuming $\Delta$ to be constant over the region of $d$-wave functions, the $q$-dependence of $d$-terms is decided by the integral $\langle \vec{k} + \vec{q} | d \rangle$. Approximating $d$-wave function by $3d$ hydrogenic wave function,

$$\langle \vec{k} + \vec{q} | d \rangle = \frac{1}{\Omega_0} \int \frac{\sin qr}{qr} \beta r^2 e^{-r/a} 4\pi r^2 dr$$  \hspace{1cm} (2.121)

Here $\beta$ is a parameter and $r_d$ represents in some sense the radius of $d$-electron. $r_d$ is treated as a parameter. Now, first two terms on right hand side of Eq. (2.15) represent a simple metal pseudopotential for which we take Ashcroft's empty core model. Then for transition metal model potential will be as follows:

$$v_{\text{ion}}(q) = \frac{1}{\Omega_0} \left[\frac{4\pi xe^2}{q^2} \cos qr_c + \frac{\beta}{\left[1 + (qr_d)^2\right]^4}\right]$$  \hspace{1cm} (2.122)
It should be noted that Lai et al. [1975] had similarly constructed a pseudopotential with four parameters

\[
v_{\text{ion}}(q) = \frac{1}{\Omega_0} \left[ -\frac{4\pi ze^2}{q^2} + \frac{\beta_g}{\left[1 + (qr_c)^2\right]^2} + \frac{\beta_d}{\left[1 + (qr_d)^2\right]^2} \right]
\]  \hspace{1cm} (2.123)

These authors arbitrarily replace the last term of the above equation, real space, by \(-\frac{ze^2}{rc+d} + \beta(r) = \text{constant}\). Here, \(rc+d\) is the core radius of \(d\)-electrons. A pseudopotential form factor based on \(R\)-matrix approach [Hubbard (1967)], Wu and Ohmura (1962), Burke an Robb (1975)] can be written as

\[
\langle \bar{k} + \bar{q} \mid W \mid \bar{k} \rangle = \langle \bar{k} + \bar{q} \mid V \mid \bar{k} \rangle - \sum_{\alpha} \frac{\langle \bar{k} + \bar{q} \mid V \mid \alpha \rangle \langle \alpha \mid V \mid \bar{k} \rangle}{E_{\alpha} - E_{\bar{k}}}
\]  \hspace{1cm} (2.124)

Here \(W\) and \(V\) refer to pseudo- and real crystal-potentials, respectively. 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 slowly varying function of \(r\) in the core region, the last term for \(d\)-electrons can be approximated by the last term of our pseudopotential.

Dagens [1976] has given a model potential known as resonant model potential for \(d\)-band metals where \(x_o\) is the first 2 elements of \(J_2(qR_d)\) [see also Dagens (1977)]. The ionic model potential proposed by Dagens can be written as

\[
v_{\text{ion}}(E') = \omega_0(E') + \frac{u}{E' - \epsilon}
\]  \hspace{1cm} (2.125)

where \(E' = E - E_0\) is the energy counted from the bottom, \(E_0\) of the valence band and \(\omega_0\) is Heine-Abarenkov model [1964] potential and \(\frac{u}{E' - \epsilon}\) represents the resonance part

\[
u (\bar{q}, \bar{k}) = 4\pi A_d \gamma (k') \gamma (k) \sum_{m} Y_{2m} (k') Y_{2m} (k)
\]  \hspace{1cm} (2.126)
with \( \vec{k}' = \vec{k} + \vec{q} \). \( u \) has finite range \( R_d \) and \( \gamma(k) \) is given by

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

(2.127)

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

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

(2.128)

an approximate \( v_{\text{von}}(q) \) = simple metal model potential + \( A \) term containing some power of \( (qR_d) \) in the denominator of a constant term. Thus, the second term in our model potential has some, although quite crude, justification from resonance model potential due to Da-gens.

3. Model of Bretonnet and Silbert [1992]

In the pseudopotential theory for simple metals, the electrons are assumed to be free in between the pseudoatoms with their scattering completely described by the pseudoatom itself. Transition metals with their broad \( d \)-bands straddling the Fermi energy, are much more complicated. In this case, an incoming plane wave with the atomic \( d \)-state gives rise to a resonance in the \( \ell = 2 \) phase shift, which for a given energy \( E \) is

\[
\tan \eta_2 = \frac{\Gamma}{2(E_d - E)}
\]  

(2.129)

The \( d \)-resonance is completely specified by the resonance energy \( E_d \) which characterises the position of the \( d \)-band and by the width \( \Gamma \) which is related to the virtual bound \( d \)-state at a given ion site. The expansion in \( \frac{\Gamma}{(E_d - E)} \) should, in principle, allow the incorporation of the effects due to the \( d \)-resonance into a perturbation theory and thus extend pseudopotential theory to transition metals. There is mounting evidence that, for transition metals, a successful theory not only should express the pair potential in terms of appropriate non-local
pseudopotentials, but it must also take account of multi-ion terms resulting, at best, in non-negligible three-body contributions [Moriarty (1988, 1990), Pettifor (1989), Vyas et al. (2001)]. However, it is extremely useful and probably necessary on computational grounds to consider the proposition that "effective" pair potentials are developed which, coupled with volume terms that incorporate the effects of many-body forces, lead to a better understanding of properties of these systems.

It is assumed, in this model, that the contribution due to the nearly free electron band formed by the $s$ and $p$ bands can be separated from that obtained from $d$-bands. This $d$-band contribution can be obtained by using an inverse scattering approach giving all the features associated with $d$-bands. For $s$-$p$ contribution one can use the empty core model. The latter, which takes account of the $s$ - $d$ mixing, is based on the distorted plane wave method for deducing potential interactions from elastic scattering phase shift [Swan and Pearce (1966), Swan (1967), Oli (1988)]. It has been shown by Swan that an approximate potential may be obtained, with reasonable accuracy, from the knowledge of the $d$-phase shift by just using the first two terms of a Dirichlet series sum of short range exponential functions, namely,

$$u_c(r) = \sum_{n=1}^{2} B_n \exp \left( -\frac{r}{na} \right)$$  \hspace{1cm} (2.130)

The above potential may be either purely attractive with a repulsive core depending on the values taken up by three parameters $B_1$, $B_2$ and $a$. Since the $s$ - $d$ mixing effect is written as the sum of individual atomic terms, just as the pseudopotentials, we may spatially superpose the empty-core potential to the $s$ - $d$ mixing potential to obtain
the following bare potential

\[ v_{\text{ion}}(r) = \begin{cases} \sum_{n=1}^{2} B_n \exp \left( -\frac{r}{na} \right) & r < r_c \\ -\frac{Z_s e^2}{r} & r > r_c \end{cases} \]  

(2.131)

where \( r_c \) stands for the empty core radius and \( Z_s \) for the effective number of valence electrons per atom.

We note that the effective total potential is weak and without explicit reference to \( d \)-band width. It simply modifies the core of the empty-core model and can be treated as a perturbation. Besides the requirement that \( v_{\text{ion}}(r) \) be continuous at the core, \( r = r_c \), we impose the weak condition that its first derivative be also continuous at the core. The reason for appealing to this condition is that, physically the repulsive part of \( v_c(r) \) should not affect drastically the behaviour of the \( s \)-electrons, while the attractive part should only slightly deepen the interaction potential so as to contract the \( s \)-states making transition metals more compact and more tightly bound. Although \( d \)-states extend further away from the nucleus than typical core electrons, it is expected that \( d \)-electrons are fairly well localised on their own atoms with the ability to hop to others through the \( s - d \) mixing. Hence, \( B_1 \) and \( B_2 \) may be deduced from the values of the parameters \( a, r_c \) and \( Z_s \) through the expressions

\[ B_1 = \frac{Z_s e^2}{r_c} \left( 1 - \frac{2a}{r_c} \right) \exp \left( \frac{r_c}{a} \right) \]  

(2.132)

\[ B_2 = \frac{2Z_s e^2}{r_c} \left( \frac{a}{r_c} - 1 \right) \exp \left( \frac{r_c}{2a} \right) \]  

(2.133)

Finally the unscreened form factor \( v_{\text{ion}}(q) \) is written as

\[ v_{\text{ion}}(q) = \frac{4\pi}{\Omega_0} a^3 \left[ \frac{B_1 J_1}{(1 + a^2 q^2)^2} + \frac{8B_2 J_2}{(1 + 4a^2 q^2)^2} \right] - \frac{4\pi Z_s e^2}{q^2} \frac{1}{\Omega_0} \cos qr_c \]  

(2.134)
where $J_n$ are defined by

$$J_n = 2 - \exp\left(-\frac{\alpha}{\alpha_{\text{na}}}\right) \left\{ \frac{\alpha_{\text{na}}}{\alpha} (1 + n^2 a^2 q^2) + (1 - n^2 a^2 q^2) \right\} \frac{s_{\text{m}} q_{\text{r}}}{q r_c}$$

$$+ \left[ 2 + \frac{\alpha_{\text{na}}}{\alpha} (1 + n^2 a^2 q^2) \right] \cos qr_c \right\}$$

(2.135)

It is worth noting that, owing to its particular form, the term corresponding to the $s$ – $d$ mixing effects, tends to zero and the long wavelength limit of the screened form factor is preserved,

$$q \rightarrow 0 \quad \frac{\tilde{v}_{\text{ion}}(q)}{\epsilon(q)} \rightarrow \frac{2}{3} E_F$$

It is also useful to point out at the similarity, inside the core, between this model and the more elaborated norm-conserving pseudopotential of Bachelet et al. [1982].

In the next chapter, we give the expressions for the calculations of the properties considered here.
References


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