CHAPTER IV

DEVELOPMENT OF PRESENT MODEL

4.1 Introduction

In the present chapter we have developed the necessary theory of a semi-first principle rigid shell model for studying lattice dynamics of hcp transition and rare-earth metals. The interaction between core-core and d-shell d-shell via conduction electrons has been considered through a screened Coulomb potential. The direct Coulomb interaction between cores and d-shell electrons is essentially short range and has, therefore, been described through non pairwise type interaction extending upto third neighbour.

4.2 The Model

In the case of transition metals the atoms in a solid are assumed to be composed of three entities, (a) the conduction electrons which are spread throughout the solid, (b) a shell of outermost d-electrons and (c) the ion core, which consists of the nucleus plus the remaining core electrons which are taken to move rigidly with the nucleus. From first principles within harmonic approximation the vibrational energy of the system of atoms can be described as

\[ V = V_{c-c} + V_{d-d} + V_{c-d} - \frac{\varepsilon}{\varepsilon} \{ V_{c-e} + V_{d-e} \} \] (4.1)
where $v^{c-c}$ is the second order change in the potential energy with respect to the displacement of ion core and due to interaction between ion cores. $v^{d-d}$ is the second order change in the potential energy between d-electron shells. $v^{c-e}$ and $v^{d-e}$ are the second order changes arising from the interaction between the conduction electrons and the ion core and the shell of d-electrons respectively. $\varepsilon$ is the dielectric function arising from the interaction between the conduction electrons. Similarly $v^{c-d}$ is the change in the potential energy arising from the interaction between the ion core and its shell of d-electrons. Since ion cores are well localised the interaction between them can be taken as the Coulomb-interactions between the point charges. The interaction between the conduction electrons and the ion core and d-electrons can be considered as the interaction of the conduction electrons with the respective potentials arising from the ion-core and d-electrons.

The potential energy terms in equation (4.1) are dependent on the product of the displacements of the ion cores and d-electron charge distributions. It may therefore be written as

$$
V = v^{c-c} \left\{U(1, c) U(1', c')\right\} - v^{c-e} \left\{U(1, c) U(1', c')\right\} + v^{c-c} \left\{U(1, c) U(1', c')\right\}/\varepsilon + v^{d-d} \left\{U(1, d) U(1', d')\right\} \\
- v^{d-e} \left\{U(1, d) U(1', d')\right\} + v^{d-e} \left\{U(1, d) U(1', d')\right\}/\varepsilon + v^{c-d} \left\{U(1, c) U(1, d)\right\} 
$$

(4.2)
First three terms in (4.2) are analogous to the potential energy terms for simple metals. Let us replace these terms by $V_1$. The next three terms of equation (4.2) are due to shell of $d$-electrons. These may be replaced by $V_2$ thus:

$$V = V_1 \{U(1, c) U(1', c')\} + V_2 \{U(1, d) U(1', d')\} + V^{c-d} \{U(1, c) U(1', d')\}$$

(4.3)

$U(1, c)$ and $U(1', c')$ are the displacements of the cores designated by $c$ and $c'$ situated within 1th and 1' th unit cells. Likewise $U(1, d)$ and $U(1', d')$ are the similar terms representing displacements for the corresponding cells. The potential energy $V_1$ obviously consists of (i) core-core and (ii) core and conduction electrons interaction. The former gives rise to the short range forces whereas the later gives rise to long range forces. Likewise $V_2$ may also be regarded to consist of similar terms.

Within the Born-Oppenheimer and harmonic approximations the ionic motion is determined by Schrodinger equation (2.6):

$$\{T(R) + V(R) \phi(R)\} = E \phi(R)$$

(4.4)

where $T$ is the kinetic energy of cores and shells of $d$-electrons. The phonon frequencies $\omega^2(q)$ can be obtained as a solution of the secular determinant equation (2.20):

$$|\Phi(q) - \omega^2 I| = 0$$

(4.5)

where $I$ is the unit matrix. $\Phi(q)$ is a (6 X 6) dynamical matrix defined by
\[ D(\vec{q}) = R + S^{-1} K \]  
(4.6)

\( R \) and \( S \) both are again \((6 \times 6)\) dynamical matrices belonging to core-core and shell-shell interactions. \( K \) describes the interaction between core and its shell of d-electrons. \( S^{-1} \) is the inverse of \( S \). Thus

\[
\begin{bmatrix}
R(\vec{q}, cc) & R(\vec{q}, cc') \\
R^*(\vec{q}, cc') & R(\vec{q}, cc)
\end{bmatrix}
\]

and

\[
\begin{bmatrix}
S(\vec{q}, dd) & S(\vec{q}, dd') \\
S^*(\vec{q}, dd') & S(\vec{q}, dd)
\end{bmatrix}
\]

\[
K' = \kappa^2 \delta_{\alpha\beta}
\]

\( \delta_{\alpha\beta} = 1 \) when \( \alpha = \beta \) and zero when \( \alpha \neq \beta \).

In view of the equation (4.3) the dynamical matrices corresponding to core and shell-shell interactions are given by

\[
\begin{align*}
R_{\alpha\beta}(\vec{q}, cc') &= \frac{1}{M} \{ \sum_{l} \frac{\partial^2 V_1}{\partial \alpha(1,c) \partial \beta(1',c')} |_{0} e^{-i(\vec{q}, \vec{R}_c)} \} \\
& \quad \text{if } c = c' \\
& + \sum_{l \neq 0} \frac{\partial^2 V_1}{\partial \alpha(1,c) \partial \beta(1',c')} |_{0} e^{-i(\vec{q}, \vec{R}_c)} \\
& \quad \text{if } c \neq c'
\end{align*}
\]

(4.7)

\[
\begin{align*}
R_{\alpha\beta}(\vec{q}, cc) &= \frac{1}{M} \{ \sum_{l \neq 0} \frac{\partial^2 V_1}{\partial \alpha(1,c) \partial \beta(1',c')} |_{0} e^{-i(\vec{q}, \vec{R}_c)} \\
& \quad - \sum_{l \neq 0} \frac{\partial^2 V_1}{\partial \alpha(1,c) \partial \beta(1,c')} |_{0} e^{-i(\vec{q}, \vec{R}_c)} \} \\
& \quad \text{if } c = c'
\end{align*}
\]

(4.8)

\( \vec{R}_c \) is the equilibrium separation between \((1, c)\)th and \((1', c')\)th ions such that

\[
\vec{R}_c = (\vec{R}_{1c}^0 - \vec{R}_{1'c'}^0)
\]
Similarly

\[ S_{ab}(\vec{q}, dd') = \frac{1}{m} \sum_{l \neq d} \left[ \delta v^2 \frac{\partial^2 v^2}{\partial u_\alpha(1,d) \partial u_\beta(1',d')} \right] \delta \bigg( \vec{q}, \vec{R}_d \bigg) \]

(4.9)

\[ S_{ab}(\vec{q}, dd) = \frac{1}{m} \sum_{l \neq d} \left[ \delta v^2 \frac{\partial^2 v^2}{\partial u_\alpha(1,d) \partial u_\beta(1',d')} \right] \delta \bigg( \vec{q}, \vec{R}_d \bigg) \]

- \sum_{l \neq d', 1 \neq d} \left[ \frac{\partial^2 v^2}{\partial u_\alpha(1,d) \partial u_\beta(1',d')} \right] \delta \bigg( \vec{q}, \vec{R}_d \bigg) \]

(4.10)

where \( \alpha, \beta = 1, 2, 3 \). \( M \) and \( m \) are masses of core and shell respectively. \( \frac{\partial}{\partial} \) denotes the derivatives of potential energies evaluated when lattice is in equilibrium.

Matrix elements corresponding to core-core interaction:

The potential energy \( V_1 \) in equation (4.3) obviously consists of (a) core-core and (b) core-conduction electrons interactions. The former has the character of short range interaction whereas latter is described by long range interaction. Thus

\[ V_1 = V_1^{s-r} + V_1^{l-r} \]

(4.11)

Each core of hcp lattice has six nearest neighbours at a distance \( \left( \frac{a}{4} + \frac{a}{3} \right)^{1/2} \) lying on \( Z = \pm \frac{c}{2} \) planes and six atoms belonging (the next nearest) neighbours at a distance 'a' lying in the basal plane. There are six third neighbour atoms at a distance \( \left( \frac{c^2}{4} + \frac{4a^2}{3} \right)^{1/2} \) lying on \( Z = \pm \frac{c}{2} \) planes. The reference core in the basal plane is supposed to interact with next nearest neighbour through non central interaction having the character of general tensor force
whereas the core of non basal planes are considered to interact with the reference core through radial as well as tangential forces.

Let the displacements of the reference core with its neighbour from their normal positions be $\vec{U}_0$ and $\vec{U}_{1mn}$, the total potential energy $V_s^{S-R} |_{R_c}^1$ when expanded in a Taylor series

$$
V_s^{S-R} = \sum \left[ \frac{1}{R_c} \frac{dV_{s-R}}{dR_c} \right]_{R_c=R_j} \left[ (\vec{U}_{1mn} - \vec{U}_0) + \frac{1}{2} (\vec{U}_{1mn} - \vec{U}_0)^2 \right] + \frac{1}{2} \left[ \frac{1}{R_c} \frac{dV_{s-R}}{dR_c} \right] \left[ \vec{R}_{1mn} \cdot (\vec{U}_{1mn} - \vec{U}_0) \right]^2
$$

(4.12)

where $j = 1$ for first neighbour and 3 for third neighbour $R_{1mn}$ represents the position coordinates of neighbouring atoms in equilibrium. The higher terms in the expansion of Taylor series have been neglected. $l, m, n$ represent the direction cosines of the line joining the reference core and the nearest neighbour. In this case the first derivative of the potential energy $\left( \frac{dV_{s-R}}{dR_c} \right)_{R_c=R_j}$ is not equal to zero.

This is because our potential $V_s(1R_c^1)$ does not represent the entire potential determining the equilibrium distance $R_j$.

Let $\beta_{2c}$ and $\alpha_{2c}$ corresponding to the expressions,

$$
\left( \frac{1}{R_c} \frac{dV_{s-R}}{dR_c} \right)_{R_c=R_1} \quad \text{and} \quad \left[ \frac{1}{R_1} \frac{d}{dR_c} \left( \frac{1}{R_c} \frac{dV_{s-R}}{dR_c} \right) \right]_{R_c=R_1}
$$

for first neighbour and let $\gamma_{3c}$ and $\alpha_{3c}$ be similar quantities for third neighbour. $\alpha_{1c}$ and $\alpha_{2c}$ are the force constants.
which adequately cover core-core tensor interaction for second neighbour.

The expressions for the matrix elements corresponding to the short range part are as follows:

\[ R_{11}^{s-r}(\vec{q}, cc) = \alpha_{1c}^s [3 - (c_1 c_2 + 2c_{21})] + 6(\beta_{2c} + \gamma_{3c}) \]

\[ + 3(x_{2c} + x_{3c}) \]

\[ R_{22}^{s-r}(\vec{q}, cc) = 3\alpha_{1c}^s [1 - c_1 c_2] + 6(\beta_{2c} + \gamma_{3c}) + 3(x_{2c} + x_{3c}) \]

\[ R_{33}^{s-r}(\vec{q}, cc) = 6(\beta_{2c} + \gamma_{3c}) + \frac{9}{8} \frac{r}{a^2} (x_{2c} + x_{3c}) \]

\[ R_{12}^{s-r}(\vec{q}, cc) = \frac{r}{a} = \sqrt{3} \alpha_{1c}^s s_1 s_2 + 2i \alpha_{2c} s_{21} - 2s_1 c_2 \]

\[ R_{13}^{s-r}(\vec{q}, cc) = R_{31} = R_{23} = R_{32} = 0 \]

\[ R_{11}^{s-r}(\vec{q}, cc') = -C_{23} [3Y_{2c} D_{11}^c + 3X_{3c} D_{21}^c] \]

\[ + \gamma_{3c} (2D_4 + 4C_{21} D_{11}^*) + \beta_{2c} (2D_2 + 4C_{11} D_{11}) \]

\[ R_{22}^{s-r}(\vec{q}, cc') = -C_{23} [X_{2c} (2D_{21}^* + C_{11} D_{11}) + X_{3c} (C_{21} D_{21}^* + 2D_4)] \]

\[ + \gamma_{3c} (2D_4 + 4C_{21} D_{11}^*) + \beta_{2c} (2D_{21}^* + 4C_{11} D_{11}) \]

\[ R_{33}^{s-r}(\vec{q}, cc') = -C_{23} [\frac{3}{2} \frac{e^2}{a^2} D_{21}^* X_{2c} + \frac{3}{2} \frac{e^2}{a^2} D_{21}^* X_{2c} \]

\[ + 3 \frac{e^2}{a^2} C_{11} D_{11} X_{2c} + \frac{e^2}{a^2} (3 \frac{e^2}{a^2} D_{21}^* + \frac{3}{8} D_4) X_{3c} \]

\[ + \gamma_{3c} (2D_4 + 4C_{21} D_{11}^*) + \beta_{2c} (2D_{21}^* + 4C_{11} D_{11}) \]

\[ R_{12}^{s-r}(\vec{q}, cc') = C_{23} \sqrt{3} i [D_{21}^* S_{21} X_{3c} - D_{11}^* S_{11} X_{2c}] \]
\[ R_{13}^{s-r}(\vec{q}, \vec{c}c') = 3 \frac{q}{a} S_{23} [D_{11} S_{12} c + \frac{1}{2} D_{21}^* S_{21} x_{3c}] \]

\[ R_{23}^{s-r}(\vec{q}, \vec{c}c') = i \sqrt{3} \frac{q}{a} S_{23} [(D_{21}^* - C_{21} D_{11}) x_{2c} + (C_{21} D_{21}^* - D_{4}) \cdot \frac{x_{3c}}{2}] \]

(4.13)

where

\[ C_1 = \cos \pi K_x a, \quad C_{21} = \cos 2\pi K_x a \]
\[ C_2 = \cos \pi K_y a \sqrt{3} \]
\[ C_{23} = \cos \pi K_z c \]
\[ S_1 = \sin \pi K_x a, \quad S_{21} = \sin 2\pi K_x a \]
\[ S_2 = \sin \pi K_y a \sqrt{3} \]
\[ S_3 = \sin \pi K_z c/2 \]
\[ S_{23} = \sin \pi K_z c \]
\[ D_1 = e^{(\pi i a K_y)/N}, \]
\[ D_2^* = e^{-2\pi i a K_y)/N} \]
\[ D_4 = e^{(4\pi i a K_y)/N} \]

(4.14)

Here \( \vec{q} = 2\pi K \) is a phonon vector and

\[ x_{2c} = \frac{A_{2c}}{1 + \frac{3}{4}(\frac{q}{a})^2}, \quad x_{3c} = \frac{A_{3c}}{1 + \frac{3}{16}(\frac{q}{a})^2} \]

The matrix elements corresponding to long range part of the potential energy \( v^{1-r} \) have been obtained using screened Coulomb interaction.

In case of transition metals conduction electrons screen the potential field of core as well as shells of
d-electrons. Obviously the strength of the screening is partitioned through a parameter $P$ into two parts. For core-core interaction the screened Coulomb potential is of the form

$$v_{1-r}^{1-r}(R_c) \sim \frac{1-P}{R_c} e^{-\lambda R_c}$$  \hspace{1cm} (4.15)

where $\lambda$ is the screening parameter such that

$$\lambda = \frac{r_e}{a_o^{1/2}} K_F$$  \hspace{1cm} (4.16)

It takes value 0.353 in Bohm Pines theory and 0.814 in Thomas Fermi theory. $r_e$ is inter-electron spacing and $K_F$ is the Fermi vector. $a_o$ is the Bohr's radius.

The derivation of matrix elements for long range part is given at the end of this chapter as an appendix. In case of hcp structure these elements are as follows:

$$R_{\alpha\beta}(\bar{q}, \mathbf{0}) = (1-P) A_p \left[ \sum_{\hbar} \frac{(\bar{q} + \hbar)_\alpha (\bar{q} + \hbar)_\beta}{|\bar{q} + \hbar|^2 + \lambda^2 f(t_1)} G^2(x_i) \right]$$

$$- \sum_{\hbar \neq 0} \frac{\hbar_\alpha \hbar_\beta \{1 + \cos(\hbar \cdot \mathbf{r})\}}{|\hbar|^2 + \lambda^2 f(t_2)} G^2(x_2)$$

$$= (1-P) A_p a_{\alpha \beta}(\mathbf{q})$$  \hspace{1cm} (4.17)

$$R_{\alpha\beta}(\bar{q}, \mathbf{0}') = (1-P) A_p \left[ \sum_{\hbar} \frac{(\bar{q} + \hbar)_\alpha (\bar{q} + \hbar)_\beta}{|\bar{q} + \hbar|^2 + \lambda^2 f(t_1)} \cdot e^{i(\bar{q} + \hbar) \cdot \mathbf{r}} \right] G(x_i)$$

$$= (1-P) A_p b_{\alpha \beta}(\mathbf{q})$$  \hspace{1cm} (4.18)
where

\[ a_{\alpha \beta}(\vec{q}) = \sum_{\vec{h} \neq 0} \frac{1}{|\vec{q} + \vec{h}|^2 + \lambda^2} \frac{(\vec{q} + \vec{h})_\alpha (\vec{q} + \vec{h})_\beta}{\vec{h}_\alpha \vec{h}_\beta \{1 + \cos(\vec{h} \cdot \vec{r})\}} \ G^2(x_2) \]

\[ b_{\alpha \beta}(\vec{q}) = \sum_{\vec{h}} \frac{1}{|\vec{q} + \vec{h}|^2 + \lambda^2} \frac{(\vec{q} + \vec{h})_\alpha (\vec{q} + \vec{h})_\beta}{f(t_1)} \ e^{i(\vec{q} + \vec{h}).\vec{r}} \]

\[ \alpha, \beta = 1, 2, 3 \]

\( \vec{r} \) is the vector distance between two cores in the unit cell.

Here \( A_p \) is a parameter which depends upon the structure of the lattice. Its value is obtained in the long wavelength limit \((\vec{q} \to 0)\). For hcp structure \( A_p = \frac{\sqrt{3}}{4} a^2 c K_e \lambda^2 \)

where \( K_e \) is the bulk modulus of electron gas and \( \frac{\sqrt{3}}{4} a^2 c \) is the atomic volume. \( \vec{h} \) is the reciprocal lattice vector.

**Matrix elements corresponding to shell-shell interaction:**

Potential energy \( V_2 \) in equation (4.3) describes

(a) d-shell - d-shell interaction and

(b) d-shell - conduction electron interaction.

The former has the nature of short range interaction and is considered through tensor type force constants. \( \alpha_{1s} \) and \( \alpha_{2s} \) restricted to second neighbour only. The matrix elements are as follows:

\[ s_{11}^{s-r}(\vec{q}, \text{dd}) = \alpha_{1s} \left[ 3 - (C_{12} C_{12} + 2C_{21}) \right] \]

\[ s_{22}^{s-r}(\vec{q}, \text{dd}) = 3\alpha_{1s} \left[ 1 - C_{12} C_{12} \right] \]
s_{33}^{s-r}(\mathbf{q}, \mathbf{dd}) = 0 \\
s_{22}^{s-r}(\mathbf{q}, \mathbf{dd}) = s_{21}^{s-r}(\mathbf{q}, \mathbf{dd}) = \sqrt{3} s_1 s_2 \alpha_1 s + 2i \alpha_2 s (s_{21} - 2s_1 c_2) \\
s_{13}^{s-r}(\mathbf{q}, \mathbf{dd}) = s_{31}^{s-r}(\mathbf{q}, \mathbf{dd}) = s_{23}^{s-r}(\mathbf{q}, \mathbf{dd}) = s_{32}^{s-r}(\mathbf{q}, \mathbf{dd}) = 0 \\
and \\
s_{11}^{s-r}(\mathbf{q}, \mathbf{dd}') = s_{22}^{s-r}(\mathbf{q}, \mathbf{dd}') = s_{21}^{s-r}(\mathbf{q}, \mathbf{dd}') = s_{13}^{s-r}(\mathbf{q}, \mathbf{dd}') = 0 \\
(4.19)

S_1, S_2, C_1, C_2, C_{21} etc. have been discussed earlier in equation (4.14).

The long range part is described through a screened Coulomb potential for the shell of d-electrons. This potential is of the form \( e^{-\lambda R_d} \) in which \( \lambda \) adjusts the strength of the screening produced by conduction electrons on the shell of d-electrons.

The matrix elements corresponding to the long range part for d-shell; d-shell interaction are as follows:

\[
s_{\alpha \beta}^{l-r}(\mathbf{q}, \mathbf{dd}) = \frac{PA}{R_d} \epsilon_{\alpha \beta}(\mathbf{q}), \quad d = d'
\]

(4.20)

\[
s_{\alpha \beta}^{l-r}(\mathbf{q}, \mathbf{dd}') = \frac{PA}{R_d} \epsilon_{\alpha \beta}(\mathbf{q}), \quad d \neq d'
\]

(4.21)

Hence for core-core and shell-shell the complete matrix elements take the form

\[
R_{\alpha \beta}(\mathbf{q}, \mathbf{cc}) = R_{s-r}(\mathbf{q}, \mathbf{cc}) + R_{l-r}(\mathbf{q}, \mathbf{cc}) + \delta_{\alpha \beta} k
\]

(4.22)

\[
R_{\alpha \beta}(\mathbf{q}, \mathbf{cc}') = R_{\alpha \beta}(\mathbf{q}, \mathbf{cc}') + R_{l-r}(\mathbf{q}, \mathbf{cc}')
\]
for core-core and

\[ S_{\alpha\beta}(\vec{q}, cc) = S_{\alpha\beta}^{s-r}(\vec{q}, cc) + S_{\alpha\beta}^{s-r}(\vec{q}, cc) + \delta_{\alpha\beta} k \]  

\[ S_{\alpha\beta}(\vec{q}, cc') = S_{\alpha\beta}^{s-r}(\vec{q}, cc') + S_{\alpha\beta}^{s-r}(\vec{q}, cc') \]

for shell-shell interaction

\[ \delta_{\alpha\beta} = 1 \text{ when } \alpha = \beta \text{ and zero elsewhere.} \]

### 4.3 Elastic Constants

In the long wavelength limit (\( \vec{q} \to 0 \)), the waves are effectively propagating as in continuous medium. Secular determinant as given by equation (4.5) is compared with elasticity determinant in the long wavelength limit and the following expressions for elastic constants have been obtained:

\[ C_{11} = \frac{1}{2\sqrt{3}} \left[ \left(9\alpha_{1c} + 9\alpha_{1s} + 3\beta_{2c} + 12\beta_{3c}\right) + (4\beta_{2c} + 16\gamma_{3c}) \right] + 2K_e \]

\[ C_{12} = \frac{1}{2\sqrt{3}} \left[ \left(\frac{1}{3}(9\alpha_{1c} + 9\alpha_{1s} + 3\beta_{2c} + 12\beta_{3c}) - (4\beta_{2c} + 16\gamma_{3c}) \right) \right] + 2K_e \]

\[ C_{13} = \frac{\sqrt{3}}{2} \left[ \left(\frac{\beta_{2c} + \gamma_{3c}}{2} - 2(\beta_{2c} + \gamma_{3c}) \right) \right] + 2K_e \]

\[ C_{14} = \frac{\sqrt{3}}{2} \left[ \left(\frac{\beta_{2c} + \gamma_{3c}}{2} + 2(\beta_{2c} + \gamma_{3c}) \right) \right] \]
\[ c_{44} = \frac{1}{\sqrt{3}c} \left[ \frac{3}{2} \frac{G}{a} x_{2c} + \frac{3}{4} \frac{G}{a} x_{3c} + 2\beta_{2c} + 8\gamma_{3c} \right] \quad (4.28) \]

\[ c_{33} = \frac{1}{\sqrt{3}a} \left[ \frac{9}{4} \frac{G}{a} x_{2c} + \frac{9}{16} \frac{G}{a} x_{3c} + 3(\beta_{2c} + \gamma_{3c}) \right] + 2K_e \quad (4.29) \]

4.4 **Equilibrium Condition and Cauchy Discrepancy**

In this model Cauchy discrepancy is defined by

\[ c_{13} - c_{44} = 2K_e - 2\sqrt{3} \frac{G}{a} \left( \beta_{2c} + \gamma_{3c} \right) \quad (4.30) \]

The condition of lattice equilibrium may be determined by the minimisation of \( V \) with respect to lattice parameters \( a \) and \( c \). These conditions are

\[ \frac{\partial V}{\partial a} = 0 \quad \text{and} \quad \frac{\partial V}{\partial c} = 0 \]

Assuming the electron pressure \( P^E \) to be isotropic we can conclude that \( V^E \) will depend on \( a \) and \( c \) only through unit cell volume,

\[ \frac{\partial V^E}{\partial a} = \frac{\partial V^E}{\partial c} = P^E \quad \text{(say)} \]

The pressure \( P^C \) exerted by core and d-shell is given by

\[ \frac{\partial V^C}{\partial a} = P^C \]

So

\[ (P^C)_c + P^E = 0 \]

and
\[(P^c)_a + P^E = 0\]

The two values of \(C_{44}\) in the above conditions give

\[\left(\beta_2c + 4\gamma_3c\right) + \frac{\sqrt{3}}{2} c P^E = 0 \quad (4.31)\]

\[\left(\beta_2c + \gamma_3c\right) + \frac{a^2}{\sqrt{3}c} P^E = 0 \quad (4.32)\]

The pressure exerted by the electron gas is assumed to be \(P^E = \frac{6}{5} K_e\). Thus the following equilibrium conditions are obtained

\[\left(\beta_2c + 4\gamma_3c\right) + \frac{\sqrt{3}}{2} c \frac{6}{5} K_e = 0 \quad (4.33)\]

and

\[\beta_2c + \gamma_3c + \frac{a^2}{\sqrt{3}c} \frac{6}{5} K_e = 0 \quad (4.34)\]

eliminating \(K_e\) from equations (4.33) and (4.34), we get

\[\beta_2c + 4\gamma_3c = \frac{3}{2}(c) \left(\beta_2c + \gamma_3c\right) \quad (4.35)\]

This is the equilibrium condition of Collins\(^{31}\) for vanishing internal stress.

Equations (4.30) and (4.35) give

\[C_{13} - C_{44} = 4.4 K_e \quad (4.36)\]

It is evident that threebody unpaired as well as volume dependent long range forces contribute to Cauchy discrepancy.
4.5 Appendix

Matrix elements corresponding to long range part of crystal potential energy:

The metal is pictured to consist of a series of point ions immersed in a free electron gas. Let \( \mathbf{R}^0(1, k) \) represents the equilibrium position of the \( k \)th ion in \( l \)th cell and \( \mathbf{R}(1, k) \) its displaced position

\[
\mathbf{R}(1, k) = \mathbf{R}^0(1, k) + \mathbf{u}(1, k)
\] (4.37)

where \( \mathbf{u}(1, k) \) being displacement.

The displacement of the \((1, k)\)th atoms from its equilibrium position produces a change in the electrostatic potential at \( \mathbf{r} \). This change is

\[
Z_k e \left[ V_i \{ \mathbf{r}_i - \mathbf{R}(1, k) \} - V_i \{ \mathbf{r}_i - \mathbf{R}^0(1, k) \} \right]
\]

The force exerted on the \((1', k')\) ion with charge \( Z_k, e \) is then given by

\[
\mathbf{F} = - Z_k Z_k' e^2 \nabla \left[ V_i \{ \mathbf{r}_i - \mathbf{R}(1, k) \} - V_i \{ \mathbf{r}_i - \mathbf{R}^0(1, k) \} \right]
\]

\[
= - Z_k Z_k' e^2 \nabla \mathbf{v}(\mathbf{r}) \cdot \mathbf{u}(1, k)
\]

\[
\mathbf{F} = - \nabla \{ Z_k Z_k' e^2 \mathbf{v}(\mathbf{r}) \} \cdot \mathbf{u}(1, k)
\]

\[
= - \nabla \{ \mathbf{v}(\mathbf{r}) \} \cdot \mathbf{u}(1, k)
\]

\[
= - V_{\alpha\beta} \mathbf{u}(1, k)
\] (4.38)

where \( \mathbf{r} = \mathbf{R}^0(1', k') - \mathbf{R}^0(1, k) \) is the equilibrium separation between \((1, k)\) and \((1', k')\).
\[ v(\vec{r}) = Z_k Z_{k'} e^2 v_i(\vec{r}) \] is the potential energy of the pair of ions \((1, k)\) and \((1', k')\) and \(V_{\alpha\beta} = \nabla^2 v(\vec{r})\) is the force constant matrix.

For a screened charge interaction potential is of the form \(r^{-1} e^{-\lambda(K) \cdot \vec{r}}\) where \((K)\) is known as the screening parameter. As the calculation of the force constant matrix is carried out conveniently in the momentum space, it becomes necessary to work with the Fourier transform of the said potential is given by

\[ v(\vec{r}) = \frac{4\pi}{(2\pi)^3} Z_k Z_{k'} e^2 \int \frac{\exp(i\vec{K} \cdot \vec{r})}{|\vec{K}|^2 + \lambda^2(K)} \, dk \] (4.39)

In practice, this expression is correct with the screening parameter calculated for the actual crystal in the presence of the appropriate periodic potential.

The long range matrix element is then given by

\[ [D_{\alpha\beta}(q)]^{1-r} = \sum_{1} V_{\alpha\beta} \exp(-i\vec{q} \cdot \vec{r}) = \sum_{1'} \nabla^2 v(\vec{r}) \cdot \exp(-i\vec{q} \cdot \vec{r}) \] (4.40)

Substitution of equation (4.39) in (4.44) gives,

\[ [D_{\alpha\beta}(\vec{q})]^{1-r} = \sum_{1} \frac{4\pi}{(2\pi)^3} Z_k Z_{k'} e^2 \int \frac{K_\alpha K_\beta \, dk}{|\vec{K}|^2 + \lambda^2(K)} \cdot e^{i\vec{K} \cdot \vec{r}} e^{-i\vec{q} \cdot \vec{r}} \] (4.41)

To evaluate the expression (4.41) we shall have to use the following sum rule

\[ \sum_{1'} \exp[i(\vec{q} - \vec{K}) \cdot \vec{r}] = \left(\frac{2\pi}{\alpha}\right)^3 \sum_{\vec{h}} \delta(\vec{q} - \vec{K} + \vec{h}) \]
where $\mathbf{h}$ is the reciprocal lattice vector and $\Omega = \frac{\sqrt{3}}{4} a^2 c$ is the cell volume. The equation (4.41) reduces to

$$[\mathcal{D}_{\alpha \beta}(\mathbf{q})]^{\perp} = \frac{4\pi e^2 Z_k Z_k'}{\Omega} \sum_{\mathbf{h} \neq 0} \frac{(\mathbf{q}_\alpha + \mathbf{h}_\alpha)(\mathbf{q}_\beta + \mathbf{h}_\beta)}{1\mathbf{q}^2 + \mathbf{h}^2 + \lambda^2(K)} + C$$

(4.42)

where $C$ is constant determined by the boundary conditions of very small displacement invariance. Since according to this boundary condition

$$0 = \frac{4\pi e^2 Z_k Z_k'}{\Omega} \sum_{\mathbf{h} \neq 0} \frac{h_\alpha h_\beta}{1\mathbf{h}^2 + \lambda^2(K)} + C$$

So

$$C = -\frac{4\pi e^2 Z_k Z_k'}{\Omega} \sum_{\mathbf{h} \neq 0} \frac{h_\alpha h_\beta}{1\mathbf{h}^2 + \lambda^2(K)}$$

(4.43)

From the equation (4.42) and (4.43)

$$[\mathcal{D}_{\alpha \beta}(\mathbf{q})]^{\perp} = \frac{4\pi e^2 Z_k Z_k'}{\Omega} \left[ \sum_{\mathbf{h} \neq 0} \frac{h_\alpha h_\beta}{1\mathbf{h}^2 + \lambda^2(K)} \right]$$

(4.44)

Krebs modifies the expression given by Lax in the following form

$$[\mathcal{D}_{\alpha \beta}(\mathbf{q})]^{\perp} = A \left[ \sum_{\mathbf{h}} \frac{(\mathbf{q}_\alpha + \mathbf{h}_\alpha)(\mathbf{q}_\beta + \mathbf{h}_\beta)}{1\mathbf{q}^2 + \mathbf{h}^2 + \lambda^2(K)} - \sum_{\mathbf{h} \neq 0} \frac{h_\alpha h_\beta}{1\mathbf{h}^2 + \lambda^2(K)} \right]$$

(4.45)
where \( \lambda_p \) is a constant which depends on the effective charge of the ion. \( \lambda \) is the screening parameter as defined in equation (4.16). Applying the many body perturbation theory, Langer and Vosko\(^91\) showed that the screening parameter was the function of electron wavenumber \( \vec{k} \). Thus

\[
\lambda' ^2 = \lambda ^2 f(t)
\]

where

\[
f(t) = 0.5 + \frac{1 - t^2}{4t} \log_e \frac{1 + t}{1 - t}
\]

with

\[
t = \frac{\vec{q} + \vec{h} \vec{l}}{2K_F}
\]

\( K_F \) is the Fermi wavevector. It was shown by Wolls and Kohn\(^92\) that if the electron wavefunctions are treated to be Bloch type, then the free electron expression include a function \( G^2(x) \). Incorporating all these expressions in (4.45)

\[
D \alpha \beta (\vec{q}) = \lambda_p \left[ \sum_\hbar \frac{(\vec{q} \alpha + \vec{h} \alpha)(\vec{q} \beta + \vec{h} \beta)}{\vec{q} + \vec{h} \vec{l} ^2 + \lambda ^2 f(t_1)} G^2(x_1) \right.
\]

\[
- \Sigma \frac{\hbar \alpha \beta G^2(x_2)}{\vec{h} \vec{l} ^2 + \lambda ^2 f(t_2)} \left. \right] \tag{4.46}
\]

where

\[
G(x) = \frac{3(\sin x - x \cos x)}{x^3}
\]
\[ x_1 = (\dot{q} + \dot{h}) \cdot \vec{r}_e \]
\[ x_2 = \vec{h} \cdot \vec{r}_e \]
\[ t_1 = \frac{|\dot{q} + \dot{h}|}{2K_F} \]
\[ t_2 = \frac{|\vec{h} \cdot \vec{r}_e|}{2K_F} \]

and
\[ K_F = \left( \frac{9\pi}{4} \right)^{1/3} \frac{1}{\vec{r}_e} \]