CHAPTER - I

HEXAGONAL CLOSE PACKED STRUCTURE & DYNAMICAL MATRIX

1.1 INTRODUCTION:

To understand elastic, thermodynamic, optical, electrical properties of solids the study of atomic vibrations is of fundamental importance. In the last about twenty years, a large amount of work has been done in the field of lattice dynamics and this topic forms an integral part of any solid state physics course. The stimuli responsible for a rapid growth of the field are (i) on the experimental side, very refined & sensitive technique have been developed to study lattice vibrations in the solids e.g. slow neutron scattering\(^1,2\), Raman spectroscopy\(^3\), x-rays inelastic scattering\(^4,5\) (ii) on the theoretical side, the availability of large fast computers and the development of sophisticated numerical techniques have made possible to solve many complex but physically interesting problems, (iii) currently the field of lattice dynamics is not considered a self contained narrow branch of solid state physics but a field which is finding very important applications in other branches of the subject e.g. superconductivity, phase transitions, semiconductor physics etc.

In a solid the atoms are coupled to each other through interatomic forces and when the lattice waves propagate through the crystal these atoms vibrate. The, lattice vibrations in a solid are quantized and the associated quanta of energy
are called phonons. In order to study the crystal structure and phonons in the crystal, the best procedure is to impinge the thermal neutrons available from nuclear reactor on the crystal. The scattered neutron beam is then analysed in terms of phonons exchanged with the lattice for wave vectors in symmetry directions. This provides the set of phonon dispersion curves. These phonon dispersion relations can be explained only when one understands the interaction system in the solid.

1.2 STRUCTURE OF HEXAGONAL CLOSE PACKED METALS:

A given substance crystallises itself into a particular stable structure for which Helmholtz energy (E-μ) happens to be minimum. In view of this stability condition, the metals are normally found to have close packed arrangement of atoms with a high degree of coordination. Although, the close packing of atoms is possible in many ways, only two highly symmetric arrangements, namely fcc face centred cubic and hcp hexagonal close packed structures are normally found in metals.

In the present work, we have restricted ourselves only to the study of hexagonal close packed (hcp) structures. In order to understand the close packed structures, we assume the atoms as hard identical spheres arranged in a regular and symmetric manner so as to have a minimum interstitial volume.
Fig: 1.1

Fig: 1.2
In a plane having closely packed spheres, each sphere is surrounded by six others forming a regular hexagon. A second similar layer can be packed by placing the spheres above alternate interstics in first layer so that each sphere is in contact with the three spheres of the lower layer. We note that in forming the second layer only the centres of every alternative triangle in the lower plane are covered. Now for a closest packing, a third layer can be added in two ways (i) If the spheres are placed in the alternate interstics in the second layer, so that they lie directly over the spheres in the first layer, the resulting structure is called close packed hexagonal (hcp) and (ii) If spheres in the third layer are placed directly above those interstics in the first layer that are not covered by the spheres in the second layer, the resulting structure is face centred cubic (fcc). Thus the structure repeats itself after two layers in (hcp). If we represent the arrangement of first layer by A and that of second layer by B, then entire hcp structure is of the sequence AB, AB, AB, ... It is to be noted that in both the arrangement each sphere is in contact with twelve spheres, six of its own plane forming a hexagon and three each of upper and lower planes forming equilateral triangles. For both type of arrangements 0.74 of the total volume is filled by sphere. From above it is clear that hexagonal close packed structure can be considered as consisting of two interpenetrating simple hexagonal lattices. One formed by sequence A and other by sequence B of the atoms.

The primitive translation vectors $a_1, a_2, a_3$ for a hexagonal lattice are shown in Fig. 1.1. The vectors $a_1$ and $a_2$ constitute basal plane (say x-y plane), make an angle of $120^\circ$ with each other and are equal in magnitude i.e. $|a_1| = |a_2| = a$, ...
the separation of atoms in the basal plane. The third vector $|a_3| = c$, where $c$ is, the separation between AA layers in this direction. The spacing 'a' and 'c' are called lattice constants. The unit cell so formed by vectors $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ is also shown in Fig. 1.1, which is a rhombohedron of height 'c' with a base of side 'a'. Each unit cell contains two atoms. Assuming one atom to be at origin, the position vector of other atom is given by

$$\vec{r} = (1/3) \vec{a}_1 + (2/3) \vec{a}_2 + (1/2) \vec{a}_3$$

The orientation of cartesian axes with respect to hexagonal axes is shown in Fig. 1.2. The x and z axes lie along the positive directions of $a_1$ and $a_3$ respectively. The primitive translation vectors of (hcp) structure can be expressed in terms of the cartesian unit vectors as follows:

$$\vec{a}_1 = \hat{a}^i, \quad \vec{a}_2 = (-1/2) \hat{a}^i + (\sqrt{3}/2) \hat{a}^j, \quad a_3 = ck$$

The ratio $(c/a)$ is called the axial ratio. For the ideal hcp structure this ratio is $\sqrt{8/3} = 1.633$. This ideal ratio is, however, not satisfied by any of the hcp metals, the deviations are quite high. The axial ratio is lowest for Be ($c/a = 1.581$) and the highest for cadmium ($c/a = 1.885$). Magnesium ($c/a = 1.632$) and Cobalt ($c/a = 1.622$), however, tend to possess approximately the ideal axial ratio. Consequently depending upon actual axial ratio being lower or higher than the ideal value, the set of twelve nearest neighbours split into two set of nearest and next nearest neighbours each containing six atoms. For metals with $c/a < \sqrt{8/3}$ as well as for those with $c/a > \sqrt{8/3}$ the coordinates and distance of various neighbours are given in Table 1.1.
### Table - 1.1

**Distribution of neighbours in hcp metals**

<table>
<thead>
<tr>
<th>Neighbours order</th>
<th>Distance</th>
<th>Ref. Type</th>
<th>Coordinates</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c/a &lt; \sqrt{8}/3$</td>
<td>$c/a &gt; \sqrt{8}/3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 0 0</td>
<td>A</td>
<td>0 0 0 0 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>First</td>
<td>Second</td>
<td>$\frac{1}{2}(a^2/3 + c^2/4)$</td>
<td>B</td>
<td>1 0</td>
</tr>
<tr>
<td>(6)</td>
<td>(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-a/2</td>
<td>-a/2\sqrt{3} c/2</td>
<td>3</td>
<td>a/2</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>a/\sqrt{3} -c/2</td>
<td>5</td>
<td>-a/2</td>
</tr>
<tr>
<td>6</td>
<td>a/2</td>
<td>-a/2\sqrt{3} -c/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second</td>
<td>First</td>
<td>a</td>
<td>A</td>
<td>7</td>
</tr>
<tr>
<td>(6)</td>
<td>(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>a/2</td>
<td>a/\sqrt{3}/2 0</td>
<td>9</td>
<td>-a/2</td>
</tr>
<tr>
<td>10</td>
<td>-a</td>
<td>0 0</td>
<td>11</td>
<td>-a/2</td>
</tr>
<tr>
<td>12</td>
<td>a/2</td>
<td>-a/\sqrt{3}/2 0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Third
(6)
Third
(6)
\[ \frac{1}{4} \left( 4a^2 + \frac{c^2}{4} \right) \]

<table>
<thead>
<tr>
<th>B</th>
<th>13</th>
<th>a</th>
<th>a/\sqrt{3}</th>
<th>c/2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14</td>
<td>-a</td>
<td>a/\sqrt{3}</td>
<td>c/2</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>-2a/\sqrt{3}</td>
<td>c/2</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>a</td>
<td>a/\sqrt{3}</td>
<td>c/2</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>-a</td>
<td>a/\sqrt{3}</td>
<td>c/2</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>0</td>
<td>-2a/\sqrt{3}</td>
<td>-c/2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fourth</th>
<th>Sixth</th>
<th>C</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2)</td>
<td>(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

19 0 0 C
20 0 0 -C

1.3 RECIPROCAL LATTICE, BRILLOUIN ZONE, AND SYMMETRY DIRECTIONS

For hcp structure the reciprocal lattice vectors are

\[ \mathbf{b}_1 = \frac{2\pi}{a} (i + j/\sqrt{3}) , \quad \mathbf{b}_2 = \frac{4\pi}{a\sqrt{3}} j , \quad \mathbf{b}_3 = \frac{2\pi}{c} \]

---(1.3)

Fig. 1.2 shows the orientation of reciprocal lattice vectors \( \mathbf{b} \) with respect to direct lattice vectors. The vector \( \mathbf{b}_1 \) makes an angle of 60° with \( \mathbf{b}_2 \) and makes an angle of 30° with \( \mathbf{a}_1 \) of direct lattice. The vector \( \mathbf{b}_3 \) lies in the direction of \( \mathbf{a}_3 \) (i.e. along positive z axis). It is obvious that the reciprocal of hexagonal direct lattice is a hexagonal lattice. In crystallographic notations, the
directions $\vec{b}_1$, $\vec{b}_2$ and $\vec{b}_3$ are represented as [11\!20], [0\!1\!10] and [0001]. Any reciprocal lattice vector $\vec{h}$ for hcp structure can be expressed in terms of the reciprocal basis vectors $\vec{b}_1$ as

$$\vec{h} = h_1 \vec{b}_1 + h_2 \vec{b}_2 + h_3 \vec{b}_3$$  

---(1.4)

Where $h_1, h_2$ and $h_3$ are integers. On substituting the value of $\vec{b}_1$ from (1.3) we get

$$\vec{h} = \frac{2\pi h_1}{a} \hat{i} + \frac{2\pi}{3} (h_1 + 2h_2) \hat{j} + \frac{2\pi h_3}{c} \hat{k}$$  

---(1.5)

The shortest and next shortest nonzero vectors are the following :-

$$\pm \frac{2\pi}{a} (i + j/\sqrt{3}), \pm \frac{2\pi}{a} (i - j/\sqrt{3}), \pm \frac{4\pi}{\sqrt{3}a} j, \pm \frac{2\pi}{c} \hat{k}$$  

---(1.6)

These are equivalent to $\pm \vec{b}_1$, $\pm (\vec{b}_1 \vec{b}_2)$, $\pm \vec{b}_2$ and $\pm \vec{b}_3$ respectively. The wigner-seitz cell in reciprocal space is known as the first Brillouin zone and is obtained by drawing perpendicular bisector planes to the shortest vectors.

The equation to these planes is

$$2q_\cdot \vec{h} + |\vec{h}|^2 = 0$$  

---(1.7)
Fig 1.3 THE FIRST BRILLOUIN ZONE OF THE HEXAGONAL CLOSE PACKED LATTICE.
Where \( \mathbf{q} \) is the wave vector defined by \( |\mathbf{q}| = \frac{2\pi}{\lambda} \).

To obtain the first Brillouin zone we draw planes which are perpendicular bisectors of vectors (non zero shortest vectors) and their equations are

\[
\pm \left| \mathbf{q}_1 \right| + \frac{1}{\sqrt{3}} \left| \mathbf{q}_2 \right| = \frac{4\pi}{3a} \\
\left| \mathbf{q}_2 \right| = \frac{4\pi}{a\sqrt{3}} \\
\left| \mathbf{q}_3 \right| = \frac{\pi}{c} \quad \text{(1.8)}
\]

These boundary planes enclose a hexagonal prism of height \( \frac{2\pi}{c} \) and base \( \frac{2\pi}{3a} \). This is therefore the first Brillouin zone of simple hexagonal lattice shown in ref. 1.3.

These planes enclose a polygon which is a right regular hexagonal prism of height \( \frac{2\pi}{c} \) and base of side \( \frac{4\pi}{\sqrt{3}a} \) and for hcp structure first Brillouin zone along with the (zone boundary points in) various symmetry directions is as shown in Fig. 1.3. The Brillouin zone for hcp lattice and hexagonal lattice are the same due to their identical translation symmetry. The calculation of phonon dispersion is much simpler in the high symmetry directions, viz. [0001], [0110] and [1120] for hcp structure. These symmetry directions also shown in Fig. 1.3. Following the group theoretical notation developed by Raghuvansh Charyulu\(^7\) for diamond structure and later applied by Iyengar et al\(^8\) to hcp structure, the zone centre is denoted by \( \Gamma \). The zone boundary points in
the [001], [0110] and [1120] directions are represented respectively by \( \Lambda M \) and \( K \). Thus the three high symmetry directions, viz [0001], [0110] and [1120] may also be expressed as \( \Gamma \Lambda \), \( \Gamma M \), and \( \Gamma KM \) directions respectively. The branches of phonon dispersion in these directions are denoted as \( \Delta, \Sigma \), \( T \) and \( T' \) where \( T \) branches lie in \( K \) and \( T' \) in \( K M \) directions. The value of \( |q_{\text{max}}| \) at zone boundary points \( \Lambda, M \) and \( K \) are respectively \( n/c, 2\pi/\sqrt{3}a \) and \( 4\pi/3a \).

Following symbols have been used in the present work according to method developed earlier.

(a) \( \Delta \) represents the symmetry direction [0001]
(b) \( \Sigma \) represents the symmetry direction [0110]
(c) \( TT' \) represents the symmetry direction [1120]
(d) \( \Gamma \) stands for the point \( \vec{q} = 0 \)
(e) \( M \) stands for the zone boundary along [0110]
(f) \( \Lambda \) stands for the boundary along [0001]
(g) \( K \) stands for the zone boundary along [1120]

1.4 SELECTION OF ALLOWED WAVE VECTORS

Using the Born's cyclic condition, the first Brillouin zone is divided into \( n \times n \times n = n^3 \) miniature cells of the basic vectors \( \frac{b_i}{n} \) (\( i = 1, 2, 3 \)). A wavevector of this miniature \( n \) cell is possible wavevector \( \vec{q} \) of the permitted
vibrations. The wavevector \( \mathbf{q} \) may accordingly be written as

\[
\mathbf{q} = n_1 \left( \frac{b_1}{n} \right) + n_2 \left( \frac{b_2}{n} \right) + n_3 \left( \frac{b_3}{n} \right) \tag{1.9}
\]

With the help of expressions (1.9), (1.10) and (1.11) we get,

\[
\mathbf{q} = \frac{2\pi}{a} \left( \frac{n_1}{n} \right) \hat{i} + \frac{2\pi}{av^3} \left( \frac{n_1 + 2n_2}{n} \right) \hat{j} + \frac{2\pi}{c} \left( \frac{n_3}{n} \right) \hat{k} \tag{1.10}
\]

where \( n_1, n_2 \) and \( n_3 \) are integers which can assume values from \(-\frac{n}{2}\) to \(\frac{n}{2}\).

Phonon wavevector \( \mathbf{q} \) in terms of its components along three rectangular axes may be written as

\[
\mathbf{q} = |\mathbf{q}_1| \hat{\mathbf{r}}_1 + |\mathbf{q}_2| \hat{\mathbf{r}}_2 + |\mathbf{q}_3| \hat{\mathbf{r}}_3 \tag{-1.11}
\]

where

\[
|\mathbf{q}_1| = \frac{2\pi}{a} \frac{n_1}{n}
\]

\[
|\mathbf{q}_2| = \frac{2\pi}{av^3} \left( \frac{n_1 + 2n_2}{2} \right)
\]

\[
|\mathbf{q}_3| = \frac{2\pi}{c} \frac{n_3}{n} \tag{-1.12}
\]

Using equations (1.8) and (1.12) the points lying on boundary of Brillouin zone are as under

\[
\begin{align*}
n_1 + 2n_2 &= \pm n \\
2n_1 + n_2 &= \pm n \tag{1.13} \\
n_3 &= \pm \frac{n}{2} \\
n_2 - n_1 &= \pm n \\
10
\end{align*}
\]
In actual practice due to symmetry we need to consider $1/24^{th}$ part of the Brillouin zone, all the integers $n_1$, $n_2$ and $n_3$ should be positive, so equation (1.13) gives

\[
\begin{align*}
n_1 + 2n_2 &= n \\
n &= \frac{n}{2} \\
n_2 - n_1 &= n
\end{align*}
\]  

---(1.14)

The equations (1.14) give the points lying on the boundary of $1/24^{th}$ part of Brillouin zone. The points lying within this irreducible segment are given by values $n_1$, $n_2$ and $n_3$ all positive and satisfy the conditions

\[
\begin{align*}
(2n_2 + n_1) &\leq n \\
n_3 &\leq n/2 \\
n_1 &\leq n_2 \\
n_2 &\leq n/2
\end{align*}
\]  

-----(1.15)

Following Dayal and Tripathi\textsuperscript{10} we have divided the first Brillouin zone into 1000 miniature cells taking $n$ to be 10. This gives a total of 84 points including origin in the irreducible segment. Each of the representative point is equivalent to many other similar points. From symmetry considerations, however an account is
taken of all these points to get the total number of points exactly 1000. In order to get correct number of similar points and hence statistical weight, one has to fill the whole space by polyhedra of first Brillouin zone. The observed number of points on the faces, the edges and the corners of the zone must be divided by the number of polyhedra sharing these points. The procedure for the hexagonal lattice is given below. The number of similar points corresponding to the possible set of \( n_1, n_2 \) and \( n_3 \) in the interior of the zone are as below (Figure 1.3).

<table>
<thead>
<tr>
<th>Possible sets</th>
<th>Number of similar points</th>
</tr>
</thead>
<tbody>
<tr>
<td>((n_1, n_2, n_3))</td>
<td>24</td>
</tr>
<tr>
<td>((n_2, n_2, n_3))</td>
<td>12</td>
</tr>
<tr>
<td>((O, n_2, O))</td>
<td>6</td>
</tr>
<tr>
<td>((n_2, n_2, O))</td>
<td>6</td>
</tr>
<tr>
<td>((O, n_2, n_3))</td>
<td>12</td>
</tr>
<tr>
<td>((O, O, n_3))</td>
<td>2</td>
</tr>
<tr>
<td>((n_1, n_2, O))</td>
<td>12</td>
</tr>
</tbody>
</table>

Other points on the faces, edges and corners of the Brillouin zone are represented as:

(a) **Points lying on the faces like B:** Such points satisfy the condition \( n_3 = n/2 \) and lie on the top and bottom surfaces. These points are shared by two
polyhedra. Therefore each point has to be counted as one half of a point.

(b) Points lying on the faces like C: These points lie on the lateral surface of the Brillouin zone and satisfy the condition \( n_1 + 2n_2 = n \). As each such point is shared by two polyhedra, it is counted as one half of a point.

(c) Points lying on the edges like PQ: For these points the conditions satisfied are \( n_1 + 2n_2 = n \) and \( n_3 = \frac{n}{2} \). These edges are shared by four polyhedra.

(d) The points on the edges like PR: The points for which \( n_1 = n_2 = \frac{n}{3} \) are shared by three polyhedra. Each such point is counted as one third of a point.

(e) Points on the corners of Brillouin zone: For these points \( n_1 = n_2 = \frac{n}{3} \) and \( n_3 = \frac{n}{2} \). Such points satisfying the above condition are shared by six polyhedra. Hence each point has to be counted as one sixth of a point.

In the present work we have been taken \( n \) to be 10, there are no such points on the edges like P, R or at the corners because \( n/3 \) will no longer be integer. There are points on the surfaces of the zone, each of which has to be counted as half of a point only and on the edges like P, Q at which a point has to be counted as one fourth. Details of such points and their statistical weight have been given elsewhere.
1.5 APPROXIMATIONS IN THE THEORY OF LATTICE DYNAMICS AND SECULAR DETERMINANT

The theory of lattice dynamics of metals has been an active area of research in solid state physics. A good deal of progress in understanding phonon in metals has been achieved through experimental and theoretical studies during the past seventy years following the publication of Debye\textsuperscript{11} and born \& Von Karman\textsuperscript{12} which lead the foundation of modern theory of lattice dynamics.

In metals there are several electrons interacting with ions that constitute the periodic lattice.\textsuperscript{13,14} It is therefore, imperative to resort to various approximations in our attempt to solve the problem.

1.5(a) THE ADIABATIC APPROXIMATION

A metal is regarded as an assembly of positively charged ions forming the periodic lattice and valence electrons moving through it. The core electrons are assumed to move rigidly with nuclei. The valence electrons respond to the motion of ions in such a way as to screen out the local charge fluctuations. The adiabatic approximation assumes that the electrons adjust themselves instantaneously corresponding to the positions of the nuclei in the perturbed crystal and the electronic state is deformed progressively by nuclear displacements. The adiabatic approximation allows us to decouple the motion of conduction electrons from that of ions.

The total Hamiltonian of the system can be written as
\[ H = \text{He} + H_1 \]  

where He is called electronic Hamiltonian and \( H_1 \) is the Hamiltonian for the system of bare ions. Further

\[
\text{He} = -\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_i^2} + \sum_{i,j} V_I (\hat{r}_i - \hat{R}_j) + \sum_{ij} \frac{e^2}{\hat{r}_i - \hat{r}_j} \quad -(1.17a)
\]

and

\[
H_1 = -\sum_i \frac{\hbar^2}{2M} \frac{\partial^2}{\partial R_i^2} + \sum_{1 \neq 1'} U_I (\hat{R}_1 - \hat{R}_{1'}) \quad -(1.17b)
\]

Thus Hamiltonian operator for whole system consisting of ions and electrons can be written as

\[
H = -\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r_i^2} + \sum_{i,j} V_I (r_i - R_j) + \sum_{ij} \frac{e^2}{\hat{r}_i - \hat{r}_j} \\
-\sum_i \frac{\hbar^2}{2M} \frac{\partial^2}{\partial R_i^2} + \sum_{1 \neq 1'} U_I (R_1 - R_{1'}) \quad -(1.18)
\]

Here \( m \) is the mass of electron and \( M \) is the mass of ion. \( \hat{r}_i \) represents the position of \( i \)th electron and \( \hat{R}_1 \) denotes the displaced position of 1th ion. The indices \( i \) and \( j \) run over all the valence electrons whereas \( 1 \) and \( 1' \) extend overall ions. The first term in equation (1.8) is the kinetic energy operator for the electrons, the second term for the electron ion potential and the third term represents potential due to electron electron interaction. The fourth term is the K.E. operator of ions and the last term is the potential energy of direct interaction between ions. \( V_I (r_i - R_j) \) includes exchange interaction between conduction and core electrons. Core electrons are regarded as tightly bound with the nuclei. \( U_I (R_1 - R_{1'}) \) includes Coulomb repulsion between ions and core-exchange
interaction.

The problem of determining the eigen values of Hamiltonian (1.8) is a difficult task, however the adiabatic approximation or the Born Openheimer\textsuperscript{15} approximation introduces tremendous simplification in the problem by separating the dynamical aspects of electron and ion motion in equation (1.8).

Let the eigen function for Hamiltonian \( H \) is given by

\[
\psi = \psi (r, R) \Phi (R) \quad \text{------(1.19)}
\]

where \( \psi (r, R) \) satisfies the Schrodinger equation for the electrons in a static lattice frozen with the 1th ion at \( \mathbf{R}_1 \), as given below

\[
H_e \psi (r, R) = E_e (R) \psi (r, R) \quad \text{------ (1.20)}
\]

The eigen function \( \psi (r, R) \) and eigen value \( E_e (R) \) depend on the position of ions.

Applying operator \( H \) to the crystal wave function \( \psi_q \) and using equations (1.16) and (1.18) one gets

\[
H \psi_q = H_l \psi_q + H_e \psi_q \quad \text{------(1.21)}
\]

\[
H \psi_q = \psi (r, R) \left[ \sum_{l=1}^{2} \frac{\hbar^2}{2M} \frac{\partial^2}{\partial R_l^2} + \sum_{l \neq 1'} U_l (R_l - R_{1'}) \right]
\]

\[
+ E_e (R) \Phi (R) - \sum_{l} \frac{\hbar^2}{2M} \left[ 2 \frac{\partial \psi}{\partial R_l} \frac{\partial \theta}{\partial R_l} + \frac{\partial^2 \psi}{\partial R_l^2} \right] \Phi (R) \quad \text{------(1.22)}
\]
If the last summation in equation (1.22) deleted we can solve our complete
eigen value problem $H \psi_q = \mathbf{E}_q \psi_q$ by making $\phi(R)$ satisfy a Schrodinger type
equation

$$[\sum_{l \neq 1} \frac{k^2}{2M} \frac{\partial^2}{\partial R_l^2} + \sum_{l \neq 1} U_{l1} (R_l - R_{1l}) + E_e (R)] \phi(R) = \mathbf{E}_q \phi(R) -----(1.23)$$

Equation (1.23) represents the Schrodinger equation for ions alone. It shows that
the motion of an ion is governed by the effective potential

$$[\sum_{l \neq 1} U_{l1} (R_l - R_{1l}) + E_e (R)].$$

Obviously electrons contribute adiabatically to the lattice energy.

The justification of this approximation can be understood by knowing the
magnitudes of different terms neglected in equation (1.22). The last term of
equation (1.22) contains two factors. We can easily prove that they contribute
almost nothing to the expectation value of energy of the system in the state $\psi_q$.
The first factor of last term vanishes as it produces integral like

$$\int \psi \frac{\partial \psi}{\partial R_l} d\tau = \frac{1}{2} \frac{\partial \psi \psi^*}{\partial R_l} d\tau$$

$$= \frac{1}{2} \frac{\partial n_e}{\partial R_l}$$

where $n_e$ is the total number of electrons. In the same way the second factor of
last term is small in view of the fact that the electrons are tightly bound to
their ions

$$\psi (r_i - R_l) = \psi (r_i - R_1)$$

It gives a contribution like.
\[ - \int \psi * \hbar^2 \frac{\partial^2}{\partial R^2} \psi \, d\tau = - \frac{m}{M} \int \psi * \hbar^2 \frac{\partial^2}{\partial r^2} \psi \, d\tau \]

so it is kinetic energy of electrons multiplied by \( \frac{m}{M} \) but \( \frac{m}{M} \) is \( 10^{-5} \) so entire contribution can be neglected in comparison to ordinary thermal energies.

In this approximation the electrons respond so quickly to the motion of the ions that their state is always a function of ionic coordinates. The adiabatic approximation allows us to separate ionic motion from the electronic motion leaving only a residual interaction between electrons and phonons. So we can treat the electrons and lattice waves as nearly independent entities and can assign for electrons and ions the same coordinates.

1.5 (b) HARMONIC APPROXIMATION:

In the harmonic approximation the potential energy of crystalline solid is expanded in powers of the amplitude of atomic vibrations and the terms higher than the quadratic are neglected. The crystal lattice with a basis is assumed to have no vacancies, dislocations and impurities.

The equilibrium position of kth ion in the 1th cell is given by

\[ \rightarrow^0 \quad R (1, k) = R (1) + R (k) \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (1.24) \]

where \( R (k) \) denotes the equilibrium position of kth ion with respect to the cell while \( R (1) \) is the position of origin of 1th cell. The ions execute small oscillations about their equilibrium positions at finite temperature because of
thermal agitation. If the displacement of the \((1, k)\)th ion from the equilibrium position be \(\mathbf{u}(1,k)\), so the displaced position of ion is given by

\[
\mathbf{R}(1, k) = \mathbf{R}_{0}(1, k) + \mathbf{u}(1,k) \quad -----(1.25)
\]

Distance between the kth ion in the lth cell and k'th ion in l'th cell at any moment is given by

\[
\mathbf{R}(1, k) - \mathbf{R}(1', k') = \mathbf{R}_{(k,k')}, \quad -----(1.26)
\]

The potential \(V\) of the whole lattice will be function of \(\mathbf{R}_{(1,1')}\) as two ions vibrate about their equilibrium positions. The total energy of the lattice

\[
T = \frac{1}{2} \sum_{1,k,\alpha} M_{k} \mathbf{u}_{\alpha=\mathbf{x,y,z}}(1, k) \quad -----(1.27)
\]

If the displacement \(\mathbf{u}(1,k)\) is smaller than the interatomic spacing the potential energy may be expanded in powers of \(\mathbf{u}(1, k)\) in Taylor's series. Because of rapid convergence series, higher terms than second order of \(\mathbf{u}(1, k)\) are neglected.

If \(V\) is the total potential energy due to nuclear displacement, then under this approximation

\[
V(\mathbf{R}) = V_{0} + V_{1} + V_{2} \quad -----(1.28)
\]

where \(V_{0}\) = equilibrium potential energy of the crystal

\[
V_{1} = \sum_{1,k,\alpha} V_{\alpha}(1, k) \mathbf{u}_{\alpha}(1, k) \quad -----(1.29a)
\]

where

\[
V_{\alpha}(1, k) = \frac{\partial V}{\partial \mathbf{u}_{\alpha}(1, k)} \bigg|_{0} \quad -----(1.29b)
\]

also
\[ V_2 = \frac{1}{2} \sum_{\alpha, \beta} V_{\alpha \beta} (1k, 1'k') \hat{u}_\alpha (1, k) \hat{u}_\beta (1', k') \quad \text{---(1.29c)} \]

where

\[ V_{\alpha \beta} = \frac{\partial^2 V}{\partial u_\alpha (1, k) \partial u_\beta (1', k')} \bigg|_o \]

The subscript zero shows that derivation is to be evaluated for equilibrium. \( \alpha \) and \( \beta \) are the cartesian components. \( V_\alpha (1, k) \) is the negative of the force on the ion in the direction at \( R (1, k) \) which is clearly zero. \( V_{\alpha \beta} (1k, 1'k') \) is the force constant acting on the ion at \( R (1, k) \) in the \( \alpha \)-direction when the ion at \( R (1', k') \) is displaced a unit distance along \( \beta \) direction. The equation of motion is

\[ M_k \ddot{u} (1, k) = \frac{V(R)}{u_\alpha (1, k)} \]

\[ = - \sum_{1', k', \beta} \frac{\partial^2 V}{\partial u_\alpha (1, k) \partial u_\beta (1', k')} \hat{u}_\beta (1'k') \]

\[ = - \sum_{1', k', \beta} V_{\alpha \beta} (1, k, 1'k') u_\beta (1'k') \quad \text{---(1.30)} \]

where

\[ V_{\alpha \beta} (1, k, 1'k') = \frac{\partial^2 V}{\partial u_\alpha (1, k) \partial u_\beta (1'k')} \bigg|_o \]

The solution of equation (1.30) can be obtained by running wave of the form as given below as there exists the periodicity of the lattice. The wave is

\[ \ddot{u}_\alpha (1, k) = \frac{u_\alpha (k)}{\sqrt{M_k}} \exp \left[ -i \{ \omega(\vec{q}) t - \vec{q}.\vec{R}(1, k) \} \right] \quad \text{---(1.31)} \]
where $\omega$ is the frequency and $q$ is propagation vector with magnitude $2\pi/\lambda$, $\lambda$ being the wavelength. We assume here that all ions of type $k$ vibrate with the vector amplitude $\mathbf{u}(k)$ which is independent of $l$.

Substituting the value of $u(k)$ and its second time derivative in equation (1.30) we get

$$M_k \omega^2 \frac{1}{\sqrt{M_k}} u_\alpha(k) = \sum_{1',k',\beta} \mathbf{V}_{\alpha\beta} u_\beta(k') \exp \left[ -i q \cdot \{ R(1,k) - R(1',k') \} \right]$$

or

$$\omega^2(q) u_\alpha(k) = \frac{1}{\sqrt{M_k M_{k'}}} \sum_{1',k',\beta} \mathbf{V}_{\alpha\beta} u_\beta(k') \exp \left[ -i q \cdot \{ R(1,k) - R(1',k') \} \right].$$

Let us define

$$D_{\alpha\beta}(q, kk') = \frac{1}{\sqrt{M_k M_{k'}}} \sum_{1',k',\beta} \mathbf{V}_{\alpha\beta} \exp \left[ -i q \cdot \{ R(1,k) - R(1',k') \} \right]$$

so that

$$\sum_{k',\beta} D_{\alpha\beta}(q, kk') u_\beta(k') - \omega^2 u_\alpha(k) = 0$$

$$\sum_{k',\beta} D_{\alpha\beta}(q, kk') - \omega^2 \delta_{\alpha\beta} \delta_{kk'} u_\beta(k') = 0$$

where $\delta_{\alpha\beta}$ and $\delta_{kk'}$ are Kronecker deltas. In the matrix notation (1.34) can be written in the form

$$[D(q) - \omega^2 \mathbf{I}] u(k) = 0$$
The matrix $D(q)$ is called Dynamical matrix and $D_{\alpha \beta}(q, kk')$ are its elements. This matrix is Hermitian in nature. $I$ is a unit matrix and $u(k)$ a column matrix. The condition that the set of equations represented by equation (1.35) have a nontrivial solution is that the determinant of the coefficients must vanish. Hence

$$\det \left( D(q) - \omega^2 I \right) = 0$$  \hspace{1cm} (1.36)

This is called secular determinant. The matrix $D(q)$ is of order $(6 \times 6)$ in hcp structure.

1.6 THE SELF CONSISTENT FIELD APPROXIMATION

In the pseudopotential theory the most crucial approximation to be made is the self consistent field approximation. The electrons in a metal form a kind of gas which is different from the perfect gas because of strong interactions of electrons among themselves and also with the positive ions. Due to large interaction, a gas of this kind must be too complicated for simple calculations. However in quantum mechanics the effect of one electron on all others to a large extent can be averaged and so each electron is thought as moving in the field of other electrons. The average potential depends on the distribution of electrons and upon the states which are occupied by them. These states in turn depend upon the potential as so we must compute the potential self consistently. Lastly the only important interaction between the electrons is the Coulomb repulsion, but this is further divided into three distinct contributions.
(a) Hartree potential\textsuperscript{16} obtained by computing the time average of electron distribution and then using Poissons equation to determine the corresponding potential.

(b) The correction for the potential seen by an electron with spin is at a position \( \vec{r} \), no other electron of the same spin can lie at that point simply because of antisymmetry of the wavefunction. This effectively gives a hole in the electron distribution and gives rise to exchange interactions.

(c) The contribution arising from the correlated motion of the electron, which is known as correlation energy.

These corrections fall under the well known Hartree Fock approximation. In Hartree Fock approximation the effect of correlation has not been properly considered. On account of the use of determinantal wavefunction the correlation of parallel spins only is taken into account while the correlation due to antiparallel spin is not being considered. Such type of correlation has been considered by Seitz and Bohm and Pins.\textsuperscript{17}

1.7 FORMULATION OF THE PSEUDO POTENTIAL

Sophisticated attempts have been made in recent years to treat many electron effects which has been ignored in the Hartree Fock approximation. The proper use of this approximation, its flexibility and usefulness of the technique has been discussed in 'Modern many theory' by Anderson.\textsuperscript{18} The study of simple metals traditionally begins with the Hartree equation which is widely simplified from of true Schrodinger equation for a metal. In practice exchange and correlation effects are included in one or self consistent approximations.
The basic aim in the lattice dynamic studies is to find techniques for obtaining wavefunctions and energy dispersion relations for electron in metals. If these relations are, one can in principle calculate any property of the metal.

If wavefunction $|\psi_k\rangle$ describes the electron with crystal momentum $k$ moving in a periodic lattice with potential $V_I$, the self consistent potential due to all other electrons in the lattice is given by $V_e$ and $E_k$, the energy eigen value we seek, then one tries to solve equation

$$(T + V_I + V_e) |\psi_k\rangle = E_k |\psi_k\rangle \quad ----- (1.37)$$

The equation (1.37) is most simplified form of the true problem but the solution of above equation is very difficult. In approximate method for solution one can expand the wavefunction $|\psi_k\rangle$ in some orthogonal basis such as plane waves,

$$<\vec{r} | K \rangle = \frac{1}{\sqrt{\Omega}} e^{i\vec{k} \cdot \vec{r}} \quad ----- (1.38)$$

where $\Omega$ is the volume of the system. The energy $E_k$ is then determined by diagonalizing a Hamiltonian matrix. One hopes that the wavefunction expansion converges rather rapidly so that the resulting matrices are not too unwieldy.

Rather elegant and sophisticated techniques have been developed for solving equation (1.37). The two methods most frequently used are augmented-plane-wave (APW) method and orthogonalized-plane-wave (OPW) method. Both methods yield the energy dispersion relation known in solid state theory as band structure. In practice it is difficult to use the band structure to calculate all the important properties about solids of our interest.

The perturbation theory can also be useful method for the solution of
equation (1.37), but this suffers from a serious drawback. The deep core potential \( V_I (r) \) is strong and attractive and wavefunction \( \psi_k \) has several nodes in the core region. The oscillatory behaviour of true wavefunction shows that the electron has large K.E as it traverses the core region and so it would require many plane wave to expand such oscillatory wavefunction. However, this difficulty has been largely overcome in APW and OPW methods. The problem in application of perturbation theory, is the depth of core potential at the ion site. It is not tenable to regard this potential as perturbation in the free electron frame.

To overcome this difficulty the model potential theories have been developed.

The motivation behind all the theories is to replace the deep ion core potential by a shallow potential well \( W (\vec{r}) \). Since the potential in the core region is shallow the electron can move across the core. It means that the model wavefunction \( \phi_k (\vec{r}) = <r|\phi_k> \) is smooth. The model wavefunction is constructed in such a way as to preserve the true eigen value of the system and is generally a function of this eigen value. The equation (1.37) can be written as

\[
(\mathbf{T} + W(E_k) + V_e) |\phi_k> = E_k |\phi_k> \quad -----(1.39)
\]

Equation (1.37) as well as equation (1.39) has same value of \( E_k \). In the equation (1.39) although the dispersion relation is not changed but the metal wavefunction does not describe electron in a metal exactly and so the pseudo wavefunction \( |\phi_k> \) is to be related with true wavefunction \( |\psi_k> \). The difference
between various model potential methods is the technique used to construct $W(\vec{r})$. In the equation (1.39) the potential can be regarded as a perturbation in the free electron system. The problem now remains that of algebra to obtain perturbation expansion for both $E_k$ and $\varphi_k(\vec{r})$. From these results several metallic properties can be studied directly. The importance of the model theories is this that using perturbation theory the calculation of properties of metals can be from the first principles.

1.8 THE ORTHOGONALISED PLANE WAVE METHOD.

Pseudopotential theory as developed by Harrison and others $^{19-21}$ has been extensively used in studying various properties of metals. The phenomenological or model pseudopotential theory differs from the first principle theory by the fact that the later does not require any explicit parameter which is borrowed from experimental data.

In self consistent field approximation the electronic behaviour is obtained from a one electron Schrödinger equation of the type,

$$H \psi_i = \{T + V_I(\vec{r})\} \psi_i = E_i \psi_i$$

--- (1.40)

Here $E_i$ is the energy of ith state while $T$ is the kinetic energy operator ($-\frac{\hbar^2}{2m} \nabla^2$). $V_I(\vec{r})$ is the self consistent potential seen by each electron. The core state $\psi_{\alpha}$ with energies $E_{\alpha}$ are different from the conduction band state $\psi_k$ with energies $E_k$. The suffix $\alpha$ denotes the position of the ion as well as energy and
angular momentum quantum number of the state.

As the positive kinetic energy of the valence electron inside the atomic core is almost completely cancelled by the negative potential, the free electron like character of the electronic energy bands of simple metals allows the effect of periodic potential on the the electrons to be treated as perturbation. In the small core approximation the core states are the same as in the isolated ion but their energies $E_\alpha$ are different.

These core states are computed in Hartree-Fock approximation. Now it remains the problem of obtaining the conduction band states, by solving the eigen value equation

$$H|\psi_k> = \{ T + V_l(r) \} |\psi_k> = E_k |\psi_k>$$

---(1.41)

If the wavefunction is expanded by choosing the plane waves then large number of plane waves are needed to get reasonably correct wavefunction. According to Herring$^{13}$ an expression in terms of orthogonalized plane waves would require much fewer terms and to produce less inconvenience in the calculation.

An OPW of wavenumber $K$ may be written as

$$\text{OPW}_K = \sum_{\alpha} e^{iK.r} \psi^*_\alpha(r') \psi_\alpha(r') e^{iK.r'} d\tau'$$

---(1.42)

This is in fact orthogonal to any core state.

The normalization of plane waves is done in volume of the metal $\Omega$ such that plane waves and normalized core functions are written as kets.
\[ |K\rangle = \Omega^{-1/2} e^{i\mathbf{k}.\mathbf{r}} \quad \text{------ (1.43)} \]
\[ |\alpha\rangle = \psi_{\alpha}(r) \quad \text{------ (1.44)} \]

In which \(|K\rangle\) denotes the plane waves and \(|\alpha\rangle\) is the core wavefunctions. The normalized plane waves in this notation become as

\[ \text{OPW}_K = |K\rangle - \sum_{\alpha} <\alpha|K\rangle \quad \text{------ (1.45)} \]

where a bra \(<\alpha| = |\alpha>^\*\) and a ket facing each other represent an integral:

\[ <\alpha|K\rangle = \Omega^{-1/2} \int \psi_{\alpha}^*(r) e^{i\mathbf{k}.\mathbf{r}} d\tau \quad \text{------ (1.46)} \]

Sometimes it is very useful to write OPW in terms a projection operator \(P\) which projects any wavefunction onto the core state so we write

\[ P = \sum_{\alpha} |\alpha\rangle <\alpha| \quad \text{------ (1.47)} \]

So OPW takes the form

\[ \text{OPW}_K = (1 - P) |K\rangle \quad \text{------ (1.48)} \]

Now conduction band state can be expanded in terms of a general linear combination of OPW's

\[ \psi_k = \sum_q C_q(K) (1 - P) |K + q\rangle \quad \text{------ (1.49)} \]

When this function for \(\psi_k\) is substituted into the Schrödinger equation (1.25) we get

\[ \sum_q C_q(K) H(1 - P) |K + q\rangle = E_k \sum_q C_q(K) (1 - P) |K + q\rangle \quad \text{------ (1.50)} \]

multiplying on left by \(<K + q|\) keeping in view that

\[ H P = \sum_{\alpha} E_{\alpha} |\alpha\rangle <\alpha| \]

we get
\[ C_q \cdot (K) \frac{\hbar^2}{2m} |K + q|^2 + \sum C_q (K) \langle K + q' | V | K + q \rangle_q - \sum E_\alpha \langle K + q' | \alpha \rangle \langle K + q \rangle \]
\[ = [C_q \cdot (K) - \sum C_q (K) \langle K + q' | \alpha \rangle \langle K + q \rangle] E_k \]

This is called orthogonized plane wave (OPW) calculation.

### 1.9 THE PSEUDOPOTENTIAL AND CANCELLATION THEOREM

It was noted by Phillips and Kleinman\(^{11}\) that all the terms in the projection operator in equation (1.50) could be taken to the left side to obtain a form

\[ T\varphi_k + W\varphi_k = E\varphi_k \]

where \( w \) is called the pseudopotential and is defined by

\[ W = V(r) + \sum_\alpha (E_k - E) | \alpha > < \alpha | = V(r) + E_k - H)P \]

\( \varphi_k \) is called the pseudowave function and is defined by

\[ \varphi_k = \sum C_q (K) |K + q\rangle \]

where \( C_0 (K) = 1 \)

The equation (1.52) is called the pseudopotential equation since \( \varphi_k \) is expected to be smooth, \( w \) is expected to be small in some sense. Thus it may form the basis for the free electron like description of the state. An interesting point to be noted is that due to presence of the projection operator the
pseudopotential is not a simple potential. The pseudopotential is non local in contrast to $V(r)$, a local potential that depends only on position ($\mathbf{r}$). A non local potential means, that the potential depends not only on the scattering momentum but also on initial state number and on the scattering angle between them. This complicates the calculation based upon the pseudopotential; but the simplicity arising from the weakness of the pseudopotential far outweighs this complication for many purposes. Further it will be reasonable to approximate $W$ by local pseudopotential.

One of the important feature is the value of $W$ is small in comparison to the true potential. The potential $V_I(r)$ is attractive. The second term in the pseudopotential equation (1.53) contains the difference ($E_K - E_\alpha$) which will always be positive since the core energies $E_\alpha$ lie below $E_K$. The projection operator $P$ is essentially positive and therefore, this positive term will cancel to some extent the attractive potential $V_I(r)$. This cancellation is known as "the cancellation theorem". The net effective potential arising from the cancellation theorem is very weak and is known as the pseudopotential.

1.10 ELASTICS MATRIX:

In lattice dynamical study, the elastic constants are usually related to the interatomic force constants by two methods (i) method static deformation (ii) the method of long waves. In the former method, the elastic energy of a macroscopic crystal is calculated for the given specified static deformation which causes the displacements of the atoms from their equilibrium sites. The energy of the crystal
for those displacements is also evaluated in terms of atomic force constants. On equating these two energies, one readily obtains the relationship between elastic constants and interatomic force constants. The later method most widely used one, correlates the elastic constants and atomic force constants of the solid in the long wave length limit \( \mathbf{q} \to 0 \). In the limit \( \mathbf{q} \to 0 \) for the acoustic mode, the displacement of atoms in the unit cell are nearly equal and low frequency vibrations correspond to sound vibrations in the crystal. Treating the medium as continuum, the velocity of the sound waves in a solid is determined in terms of its macroscopic elastic constants. The velocity of sound can also be determined in terms of force constants from the solution of the secular equation (1.35). Thus the expressions for elastic constants in terms of force constants can be easily obtained.

In the long wave length limit \( q \to 0 \) the well known Christoffel equation for solids is

\[
\text{Lim } q \to 0 \left| C_{\alpha\beta\delta\rho} q_{\beta} q_{\delta} - PW^2 \delta_{\alpha\rho} \right| = 0 \quad (1.55)
\]

Number of nonzero independent elastic constants is reduced to only a few after imposing the symmetry condition of crystal structures. In the case of hexagonal structure following five non-vanishing independent constants exist

\[
C_{1111} = C_{2222} = C_{11}, \quad C_{3333} = C_{33}, \\
C_{1212} = C_{66} = 1/2 (C_{11} - C_{12}); \quad C_{1313} = C_{2323} = C_{44} \\
\text{and } C_{1133} = C_{13}
\]

(1.55) \quad (1.56)

The solution of equation (1.55) along the high symmetry directions are simple and for direction [0001] it gives
\[
\lim_{q \to 0} \frac{\rho w^2}{q^2} = C_{33} \text{ for LA mode} \quad (1.57)
\]
\[
\lim_{q \to 0} \frac{\rho w^2}{q^2} = C_{44} \text{ for TA mode}
\]

The solution is symmetry direction [0110] gives
\[
\lim_{q \to 0} \lim_{q \to 0} \frac{\rho w^2}{q^2} = C_{11} \text{ for LA mode} \quad (1.58)
\]
\[
\lim_{q \to 0} \frac{\rho w^2}{q^2} = C_{44} \text{ for TA mode}
\]
\[
\lim_{q \to 0} \frac{\rho w^2}{q^2} = \frac{1}{2} (C_{11} - C_{12}) \text{ for TA}_{11} \text{ mode}
\]

The expression for fifth elastic constant \(C_{13}\) is obtained by transforming the dynamical matrix into centre of mass system and then solving the secular determinant in direction [0110] for long wave length limit and considering (2,3) elements\(^{22}\).

It is to be noted that we get two different expressions for \(C_{44}\) as we approach the limit \(q \to 0\) along [0001] and [0110] symmetry directions which become identical in the light of rotational invariance condition of the crystal.

1.11 CRYSTAL EQUILIBRIUM CONDITIONS:

The real crystals with which we deal in our studies are of finite size and the irregularities existing at the boundary have a little effect on the bulk properties of the crystal. However, for lattice dynamical studies we treat the
crystal to be of infinite dimensions in all directions. In order that a finite lattice may be treated as infinite certain restrictions have to be imposed on it. One such restriction is that all the displacements in the infinite lattice must be specified like a finite lattice, with respect to the equilibrium positions of the ions, measured in absence of any external force. The restrictions impose on infinite lattices are known as equilibrium conditions and are realized if

(i) Every ion is in equilibrium position and (ii) the configuration correspond to vanishing stress.

A separate fulfilment of the above two conditions is necessary because an equilibrium configuration is not necessarily free of external stresses. These conditions are automatically satisfied by real finite crystals. For infinite crystal the equilibrium conditions are analytically deduce by the theory of homogeneous deformation of the lattice, which ultimately end up in the following two sets of equilibrium conditions necessary for the crystal

\[ \Sigma_{1',k'} V(1', kk') X_\alpha (1', kk') = 0 \]  \hspace{1cm} (1.59)

\[ \Sigma_{kk'} V(1', kk') X_\alpha (1', kk') X_\beta (l', k'k) = 0 \] \hspace{1cm} (1.60)

Where \( V(l, kk') \) denotes the first order space derivative of potential between two atoms situate at positions (l'k') and (ok) respectively. \( X_\alpha (o, k, l'k') \) denotes the relative coordinate of atom (l'k') w.r.t. the atom at the origin.
If we sum the terms of left hand side of equation (1.30) over all the values of k, the results identically vanish i.e. out of r equations for each value of k only (r-1) are independent, and hence equation (1.60) represent a set of 3 (r-1) mutually independent equations (where r denotes the number of atoms per unit cell).

Further equation (1.60), symmetric in Cartesian indices α and β, represents a set of six independent equations. Thus above two sets of equations represent in all 3 (r+1) independent equations as the equilibrium conditions for the infinite lattice. Owing to the symmetry of structure these 3(r+1) equations are reduced to one or two independent equations.

1.12 HUANG’S COMPATIBILITY CONDITIONS:

The set of equilibrium conditions (1.59) and (1.60) deduced above merely satisfy the condition (i) and (ii) and the system is not necessarily free of stresses. Huang has pointed out that a more satisfactory and general set of conditions can be obtained by the method of long waves (q→0). In long wave length limit acoustic vibrations of the lattice represent elastic waves in the solid. This not only introduces elastic constants in the solid. This not only introduces elastic constants in the theory but also gives expressions for anisotropic stresses in the configuration with respect to which are defined the derivatives of interatomic potential and enable one to impose equilibrium conditions for stress to vanish. Huang has established that the system, in order to be free of
stresses, must satisfy the following symmetry relations known as Huang’s compatibility condition w.r.t. the Cartesian indices $\alpha, \beta, \gamma, \lambda = 1,2,3$,

$$[\alpha\beta, \gamma\lambda] = [\alpha\beta, \lambda\gamma] = [\beta\alpha, \gamma\lambda] = [\beta\alpha, \lambda\gamma] \quad \text{(1.61)}$$

with symbols and brackets having their usual meaning. In content of the central pairwise potential, the equilibrium conditions (1.59) becomes.

$$V_\alpha (k) = 2 \sum_{lk} V (x_\alpha)_{x(l',kk')} = 0 \quad \text{---(1.62)}$$

While the equilibrium condition (i) now becomes.

$$\sum_{kk'} [V'(x_\alpha x_\beta)]_{x(k,k',l') \text{ etc}} = 0 \quad \text{---(1.63)}$$

Which is identical to equilibrium condition (1.60) and is also the condition of rotational invariance. Thus Huang’s method of long waves leads to the same set of equilibrium conditions as deduced by the minimisation of crystal energy density.

1.13 **EQUILIBRIUM CONDITION FOR HCP STRUCTURE:**

A detailed description of hcp structure has been given in Sec (1.2). The two atoms of type $k=1$ and $k=2$ belonging to unit cell are situated at position $(O,O,O)$ and $(O, \frac{\sqrt{3}}{2} a, \frac{c}{2})$ respectively with respect to the atom of type $k=1$ at origin, the distance of various neighbours are as follows:

$$r_1 = (\frac{a^2}{3} + \frac{c^2}{4})^{1/2}; \quad r_2 = a; \quad r_3 = (\frac{4a^2}{3} + \frac{c^2}{4})^{1/2}$$

If we designate the number of neighbours by $j$, the sum over $\lambda, k$ and $\beta, k'$ etc can be replaced by the sum over 2 indices only, one denoting the different sets of neighbours and other members of each neighbours. The symmetric hcp
structure straightforwardly suggests that for $\alpha \neq \beta$ the two sets of equilibrium conditions (1.62) and (1.63) are automatically satisfied, while for $\alpha = \beta$ relations (1.62) and (1.63) lead to the following equilibrium conditions

$$\sum \sum [V^1(x_j^2)]_{x(j)} = 0$$

and

$$\sum \sum [V^1(x_j^2)]_{x(j)} = 0 \quad \text{-----(1.64)}$$

On substituting values of $x(j)$ from Table 1.1 the two relations may be explicitly written as

$$V^1_1(r_1) + 3V^1_2(r_2) + 4V^1_3(r_3) + = 0 \quad \text{-----(1.65)}$$

and

$$V^1_1(n) + V^1_3(r_3) + = 0 \quad \text{-----(1.66)}$$

These equilibrium conditions for hcp structure can equivalently be written as

$$\frac{\partial V}{\partial a} = 0$$

$$\frac{\partial V}{\partial c} = 0 \quad \text{-----(1.67)}$$

where

$$V = 1/2 \mid 6V^1_1(r_1) + 6V^1_2(r_2) + 6V^1_3(r_3) + \cdots \mid$$

is the total interaction potential per ion. The conditions (1.66) and (1.67) have been deduced in the condition of vanishing external stress when $\alpha = \beta = 1, 2$ and $\gamma = \lambda = 3$. We get for hcp structure the Huang’s condition of rotational invariance as
\[ \sum_{j \text{ jth neighbours}} \sum_{j \text{ jth neighbours}} [V x_1^2]_{x(j)} = \sum_{j \text{ jth neighbours}} [V x_2^2]_{x(j)} \]

\[ = \sum_{j \text{ jth neighbours}} [V x_3^2]_{x(j)} \quad \text{(1.68)} \]

which is equivalent to

\[ \left( \frac{\partial V}{\partial a} \right)_c = \left( \frac{\partial V}{\partial c} \right)_c \quad \text{(1.69)} \]

Thus in equilibrium an hcp lattice, force of external stress, must satisfy the condition (1.65) and (1.66) and (1.69). In such a case, for hcp system, relation (1.61) gives

\[ C_{2323} = C_{3232} \]

which means that the two expressions of \( C_{44} \) obtained from [0001] and [0110] are identical in view of condition (1.69).
REFERENCES: