Approximation Used In the Theory & The Secular Determinant

2.1 INTRODUCTION:

In the preceding chapter we have discussed the hexagonal - close-packed structure. The dynamical theory of a metallic crystal is basically a many body problem of number of electrons interacting with the ions that constitute the lattice and cannot be solved explicitly. It is, therefore, imperative to resolve to various approximations in our attempts to solve the problem. These approximations are:

(1) The adiabatic approximation

(2) The harmonic approximation

2.2 THE ADIABATIC APPROXIMATION:

A metal consists of a large number of ions. These ions form a periodic lattice with one or more electrons per ion. These electrons are completely detached from the ion forming the so called electron gas. When a thermal wave disturbs the lattice, the atoms execute small vibrations about their mean positions. It is assumed that the ions cores vibrate as rigid units. While the conduction electron move relative to them under the influence of electric fields of ions and their own. The possible frequencies for the normal modes of vibration of lattice
can be calculated by expressing the basic Hamiltonian of the lattice and then to determine its eigen values.

The Hamiltonian operator [1, 2] for the lattice consisting of ions and electrons is given by

\[ H = -\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \vec{r}_i^2} + \sum_{i,j} V_i (\vec{r}_i - \vec{R}_j) + \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_i \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \vec{R}_i^2} + \sum_{i \neq i'} U_i (\vec{R}_i - \vec{R}_{i'}) \]

(2.4)

Where
- \( m \rightarrow \) Mass of the electron
- \( M \rightarrow \) Mass of the ion
- \( \vec{r}_i \rightarrow \) Position vector of the \( i^{th} \) electron
- \( \vec{R}_i \rightarrow \) Displaced position vector of the \( i^{th} \) ion
- \( -\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \vec{r}_i^2} \rightarrow \) The kinetic energy operator for the electrons
- \( \sum_{i,j} V_i (\vec{r}_i - \vec{R}_j) \rightarrow \) Potential energy due to electron - ion interaction
- \( \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \rightarrow \) Potential energy due to electron-electron interaction
- \( -\sum_i \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \vec{R}_i^2} \rightarrow \) The kinetic energy operator of ions.
- \( \sum_{i \neq i'} U_i (\vec{R}_i - \vec{R}_{i'}) \rightarrow \) Potential energy due to ion-ion interaction.
In the above discussion, we have assumed that the core electrons move rigidly with nuclei to produce the bare electron-ion interaction $V_i(\vec{r}_i - \vec{R}_j)$, which includes exchange interaction between conduction and core electrons.

In order to avoid the singularities originating on account of the Coulomb interaction present in equation 2.1 the spatial average of the potential is taken to be zero and the interaction of particle with itself [3] is included. To obtain eigen values corresponding to the Hamiltonian (equation 2.1) we use adiabatic or Born Openheimer [4] approximation.

The total Hamiltonian may be expressed as

$$H = H_i + H_e$$ (2.2)

Where

$$H_i = -\sum_i \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \vec{R}_i^2} + \sum_{l=1} U_i(\vec{R}_i - \vec{R}_r)$$ (2.3)

and

$$H_e = -\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \vec{r}_i^2} + \sum_{l=1} V_i(\vec{r}_i - \vec{R}_L) + \sum_{l=1} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$ (2.4)

Let the eigen function for the Hamiltonian $H$ be

$$\Psi_q = \psi(\vec{r}, \vec{R}) \phi(\vec{R})$$ (2.5)

Using equations 2.2 and 2.5 we write

$$H \Psi_q = H_i \Psi_q + H_e \Psi_q$$

$$= H_i \Psi_q + H_e \{ \Psi(\vec{r}, \vec{R}) \phi(\vec{R}) \}$$

$$= H_i \Psi_q + \phi(\vec{R}) H_e \Psi(\vec{r}, \vec{R})$$ (2.6)
where \( \psi(\bar{r}, \bar{R}) \) satisfies the Schrödinger equation for the electrons in a static lattice frozen with the \( I^{th} \) ion at \( \bar{R}_i \), as given below;

\[
H_e \psi(\bar{r}, \bar{R}) = E_e(\bar{R}) \psi(\bar{r}, \bar{R}) \tag{2.7}
\]

\( E_e(\bar{R}) \) is the eigen value corresponding to the wave function \( \psi(\bar{r}, \bar{R}) \).

These eigen values are the functions of ionic positions.

Now applying the operator \( H_1 \) to the crystal wave function \( \psi_q \) and using equation 2.7 we get

\[
H_1 \Psi_q = \left[ -\sum_{i=1}^{n} \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \bar{R}_i^2} + \sum_{i=1}^{n} U_i(\bar{R}_i - \bar{R}_f) \psi(\bar{r}, \bar{R}) \phi(\bar{R}) \right] \tag{2.8}
\]

\[
\psi(\bar{r}, \bar{R}) \phi(\bar{R}) + \sum_{i=1}^{n} U_i(\bar{R}_i - \bar{R}_f) \psi(\bar{r}, \bar{R}) \phi(\bar{R})
\]

Now from equations 2.6, 2.7 and 2.8 we get

\[
4 \Psi_q = \psi(\bar{r}, \bar{R}) \left[ -\sum_{i=1}^{n} \frac{\hbar^2}{2M} \frac{\partial^2}{\partial \bar{R}_i^2} + \sum_{i=1}^{n} U_i(\bar{R}_i - \bar{R}_f) + E_e(\bar{R}) \right] \psi(\bar{r}, \bar{R}) \phi(\bar{R}) \tag{2.9}
\]

\[
-\sum_{i=1}^{n} \frac{\hbar^2}{2M} \frac{\partial \psi}{\partial \bar{R}_i} \frac{\partial \phi}{\partial \bar{R}_i} + \frac{\partial^2 \psi}{\partial \bar{R}_i^2} \phi(\bar{R})
\]

The term of third line in equation 2.9 contributes almost nothing to the expectation values of the system in the state \( \psi_q \). The first term of the third line vanishes because it produces integrals, like
Where $n_e$ is the total number of electrons

Thus,

$$\int \psi^* \frac{\partial \psi}{\partial R_1} \, d\tau = 0 \quad (2.10)$$

The second term in the third line of equation 2.9 is very small because at worst the electrons would be tightly bound to their ions.

Thus,

$$\psi(\vec{r}_1, \vec{R}_1) = \psi(\vec{r}_1 - \vec{R}_1)$$

Which would give a contribution like

$$- \int \psi^* \frac{\hbar^2}{2M} \frac{\partial^2 \psi}{\partial R_1^2} \, d\tau = - \frac{m}{M} \int \psi^* \frac{\hbar^2}{2M} \frac{\partial^2 \psi}{\partial R_1^2} \, d\tau$$

$$= - \frac{m}{M} \text{(kinetic energy of electrons)} \quad (2.11)$$

Since $\frac{m}{M}$ is of the order of $10^{-4}$ or $10^{-5}$,

Hence - $\int \psi^* \frac{\hbar^2}{2M} \frac{\partial^2 \psi}{\partial R_1^2} \, d\tau$ is negligibility small.

So with the help of equations 2.10 and 2.11 the equation 2.9 may be written as follows:

$$H \Psi = \psi(\vec{r}, \vec{R}) \left[ - \sum_i \frac{\hbar^2}{2M} \frac{\partial^2 \phi}{\partial R_i^2} + \sum_{i \neq j} U_1(\vec{R}_1 - \vec{R}_1) + E_e(\vec{R}) \right] \phi(\vec{R}) \quad (2.12)$$
Now we can solve the complete eigen value problem, 

$$H\psi_q = E_q \psi_q,$$

by making $\phi((\tilde{R}))$ satisfy a Schrodinger type equation.

$$\left[ -\sum_{l} \frac{\hbar^2}{2M} \frac{\partial^2}{\partial R_i^2} + \sum_{l \neq l'} U_1(\tilde{R}_1 - \tilde{R}_f) 
+ E_e(\tilde{R}) \right] \phi(\tilde{R}) = E\phi(\tilde{R})$$

(2.13)

The above equation is for the wave function of the ions alone, which shows that the motion of ions is governed by the effective potential $E_e(\tilde{R}) + \sum_{l \neq l'} U_1(\tilde{R}_1 - \tilde{R}_f)$ i.e. electrons contribute adiabatically to the lattice energy.

In the adiabatic approximation electrons respond so quickly to the motion of the ions that their state is always just a function of the ionic coordinates. Thus, in this approximation we can separate the ionic motion from the electronic motion, leaving only a residual interaction between the electron and the phonons. So we can treat the electrons and lattice waves as nearly independent entities and allot the electrons the same co-ordinate as that of ions.

2.3 THE HARMONIC APPROXIMATION:

In this approximation the potential energy of a crystalline solid is expanded in powers of the amplitude of the atomic vibrations and all terms higher than these which are quadratic in amplitude are neglected.

Let us suppose, $\tilde{R}^o(I.K)$ - The position vector of the $K^{th}$ ion in the $1^{th}$ cell in equilibrium position.
\( \mathbf{R}^o (I) \) - The position vector of the origin of the \( I^{th} \) cell.

\( \mathbf{R}^o (k) \) - The position vector of the \( K^{th} \) ion with respect to the cell, in equilibrium position.

Thus, \( \mathbf{R}^o (I,k) = \mathbf{R}^o (I) + \mathbf{R}^o (k) \) (2.14)

Let the \((I,K)\) ion be displaced by a displacement \( \mathbf{u} (I,k) \) from its equilibrium position. The displaced position vector \( \mathbf{R} (I,K) \) is given by

\[
\mathbf{R} (I,k) = \mathbf{R}^o (I,k) + \mathbf{u} (I,k)
\] (2.15)

The distance between the \( k^{th} \) ion in the \( I^{th} \) cell and \( k^{th} \) ion in the \( I^{th} \) cell at any instant is

\[
\mathbf{R} \left( \begin{array}{c} I \\ k \end{array} \right) - \mathbf{R} \left( \begin{array}{c} I' \\ k' \end{array} \right) = \mathbf{R} (I,k) - \mathbf{R} (I',k')
\] (2.16)

As the two ions vibrate about their equilibrium, positions the potential energy \( V \) of the whole lattice will be a function of \( \mathbf{R} \left( \begin{array}{c} I \\ k \end{array} \right) \). The total kinetic energy of the lattice due to thermal fluctuation of ions is given by

\[
T = \frac{1}{2} \sum_{I,k,\alpha} M_k \mathbf{\dot{U}}^2_{\alpha} (I,k)
\] (2.17)

Where \( M_k = \) Mass of the \( k^{th} \) atom.

\( U_x (I,k), U_y (I,k), U_z (I,k) \) are the components of \( \mathbf{u} (I,k) \) along \( x, y, z \) directions respectively.

Now the potential energy of the crystal.
\[ V(\tilde{R}) = V \{ \tilde{R}^0 + \tilde{u}(I,k) \} \]  

(2.18)

If the displacement \( \tilde{u}(I,k) \) is smaller than the interatomic spacing, then \( V(\tilde{R}) \) can be expanded in powers of \( \tilde{u}(I,k) \) in Taylor's series. This series may be expected to converge rapidly, therefore, we are justified in neglecting the terms higher than the second power of \( \tilde{u}(I,k) \).

\[ V(\tilde{R}) = V \{ \tilde{R}^0 + \tilde{u}(I,k) \} \]

Thus,

\[ V(\tilde{R}) = V_o + \sum \left[ \frac{\partial V}{\partial u_a(I,k)} \right]_{o} \tilde{u}_a(I,k) \]

\[ + \frac{1}{2} \sum \left[ \frac{\partial^2 V}{\partial u_a(I,k) \partial u_b(I',k')} \right]_{o} \tilde{u}_a(I,k) \tilde{u}_b(I',k') \]  

(2.19)

\( V_o \) is potential energy of the crystal in equilibrium position. The subscript \( o \) means that the derivatives are evaluated for the equilibrium configuration.

\( \left( \frac{\partial V}{\partial u_a(I,k)} \right)_{o} \) may be interpreted as the negative of the force acting in the \( \alpha \) direction on the ion at \( \tilde{R}^0(I,k) \) in equilibrium configuration.

\( \left( \frac{\partial^2 V}{\partial u_a(I,k) \partial u_b(I',k')} \right)_{o} \) represent the force constant acting on the ion at \( \tilde{R}^0(I,k) \) in the \( \alpha \) direction, when the ion at \( \tilde{R}^0(I,k) \) is displaced by a unit distance by a unit distance along \( \beta \) direction.

The resultant force acting on any particles in equilibrium configuration will be zero.
So \( \left( \frac{\partial V}{\partial u_\alpha (l,k)} \right)_o = 0 \) \hspace{1cm} (2.20)

The cartesian components \( \alpha (=x,y,z,) \) of force on any ion are

\[
- \frac{\partial V (\vec{R})}{\partial u_\alpha (l,k)} = - \sum_{l',k',\beta} \left( \frac{\partial^2 V}{\partial u_\alpha (l,k) \partial u_\beta (l'k')} \right)_o \bar{u}_\beta (l'k')
\]

Thus the equation of motion are

\[
M_K u_\alpha (l,k) = - \frac{\partial V (\vec{R})}{\partial u_\alpha (l,k)}
\]

\[
= - \sum_{l',k',\beta} \left( \frac{\partial^2 V}{\partial u_\alpha (l,k) \partial u_\beta (l'k')} \right)_o u_\beta (l',k')
\]

\[
M_K u_\alpha (l,k) = - \sum_{l',k',\beta} V_{\alpha \beta} (l,k,l',k') u_\beta (l',k')
\]

(2.22)

Where

\[
V_{\alpha \beta} (l,k,l,k') = \left[ \frac{\partial^2 V}{\partial u_\alpha (l,k) \partial u_\beta (l',k')} \right]_o
\]

(2.23)

(2.24)

From the above equation we will get infinite sets of simultaneous linear differential equations. Due to periodicity of the lattice we may choose in running wave solution in the form.

\[
\bar{u}_\alpha (l,k) = \frac{1}{\sqrt{M_K}} u_\alpha (K) \exp \left\{ i \omega (\vec{q}) t - \vec{q} \cdot \vec{R}_o (l,k) \right\}
\]

\( \bar{u}_\alpha (K) \) is independent of \( l \) and \( \vec{q} \) is wave vector of the disturbance.

From Equation 2.23 and 2.25

\[
\int M_K M_K \omega^2 (\vec{q}) u_\alpha (K) = \sum_{l',k',\beta} V_{\alpha \beta} u_\beta (K') \exp \left\{ i \omega \left\{ \vec{R}_o (l,k) - \vec{R}_o (l',k') \right\} \right\}
\]

(2.26)
or \[ M_K M_K \omega^2 (q) u_{\alpha} (K) = \sum_{k_{\beta}} D_{\alpha \beta} (\bar{q}, K K') u_{\beta} (K') \] (2.27)

Where
\[ D_{\alpha \beta} (\bar{q}, K K') = \sum_{l} V_{\alpha \beta} \exp \left(-i\bar{q} \left(\bar{R}^0 (l, k) - \bar{R}^0 (l', k')\right)\right) \] (2.28)

For monoatomic hexagonal crystal
\[ M_K = M_{K'} = m \] (say)

So the equation 2.28 reduces to
\[ m \omega^2 (q) u_{\alpha} (K) = \sum D_{\alpha \beta} (\bar{q}, K, K') U_{\beta} (K') = 0 \] (2.29)

In order that the equation 2.29 may have a solution the condition is that the determinant of coefficient should vanish. Therefore the secular determinant for a monoatomic hexagonal crystal can be written as
\[ \left| D_{\alpha \beta} (\bar{q}, K K') - m \omega^2 (q) \delta_{\alpha \beta} \delta_{K K'} \right| = 0 \] (2.30)
or
\[ \left| D (\bar{q}) - m \omega^2 I \right| = 0 \] (2.31)

Where \( \delta_{\alpha \beta} \) and \( \delta_{K K'} \) are Kronecker deltas.

I is the unit matrix and the dynamical matrix \( D (\bar{q}) \) is a 6x6 matrix.

The secular determinant can be solved easily along the symmetry directions as the secular equations in these directions are factorised in three 2x2 submatrices which represent purely longitudinal or purely transverse wave solutions. However, for a given general direction the solution of secular equations is somewhat more difficult because equations do not get factorised.
In the case of hexagonal close packed structure the dynamical matrix $D(\bar{q})$ is written as

$$D(\bar{q}) = \begin{pmatrix} A(\bar{q}) & B(\bar{q}) \\ B^*(\bar{q}) & A(\bar{q}) \end{pmatrix}$$  \hspace{1cm} (2.32)

Where $A(\bar{q})$ and $B(\bar{q})$ are $3 \times 3$ submatrices and $B^*(\bar{q})$ is the complex conjugate of $B(\bar{q})$.

The submatrices $A(\bar{q})$ and $B(\bar{q})$ are defined by

$$A(\bar{q}) = \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix}$$  \hspace{1cm} (2.33)

$$B(\bar{q}) = \begin{pmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{pmatrix}$$  \hspace{1cm} (2.34)

### 2.4 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 interaction 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 others 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 [5] 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 \( \bar{r} \), no other electron of the same spin can lie at that point simply because
of antisymmetry of the wave function. 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 wave function the
correlation of parrallel spins only is taken into account while the correlation due to
antiparallel spin is not been considered. Such type of correlation has been
considered by Seitz and Bohm and Pins [6].
2.5 FORMULATION OF THE PSEUDOPOTENTIAL:

Sophisticated attempts have been made in recent years to treat many
electron effects which have 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 [7]. 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 wave functions and energy dispersion relations for electron in metals. If
these relations are, one can in principle calculate any property of the metal.

If wave function $|\psi_k>$ describes the electron with crystal momentum
$\vec{k}$ moving a periodic lattice with potential $V_F$ the self consistent potential due to all
other electrons in the lattice is given by $V_c$ and $E_k$ the energy eigen value we seek,
than one tries to solve equation

$$(T + V_I + V_c)|\psi_k> = E_k|\psi_k>$$

(2.35)

The equation (2.35) is most simplified form of the true problem but
the solution of above equation is very difficult. In approximation method for
solution one can expand the wave function $|\psi_k>$ in some orthogonal basis such as
plane waves.
Where $\Omega$ is the volume of the system. The energy $E_k$ is then determined by diagonalizing a Hamiltonian matrix. One hopes that the wave function expansion converges rather rapidly so that the resulting matrices are not too unwidely.

Rather elegant and sophisticated techniques have been developed for solving equation (2.35). 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 (2.35), but this suffers from a serious drawback. The deep core potential $V_1(r)$ is strong and attractive drawback. The deep core potential $V_1(r)$ is strong and attractive and wave function $\psi_k$ has several nodes in the core region. The oscillatory behaviour of true wave function 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 wave function. 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 wave function $\phi_k(\vec{r}) = \langle r / \phi_k \rangle$ is smooth. The model wave function 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 (2.35) can be written as

$$(T + W(E_k) + V_r)\phi_k = E_k\phi_k$$

(2.37)

Equation (2.35) as well as equation (2.37) has same value of $E_k$. In the equation (2.37) although the dispersion relation is not changed but the metal wave function does not describe electron in a metal exactly and so the pseudo wave function $|\phi_k\rangle$ is to be related with true wave function $|\psi_k\rangle$. The difference between various model potential methods is the techniques used to construct $W(\vec{r})$. In the equation (2.37) 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 $\phi_k(\vec{r})$. From these results several metallic properties can 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.

2.6 THE ORTHOGONALISED PLANE WAVE METHOD:

Pseudopotential theory as developed by Harrison [8, 9] and others [10,11] 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 Schrodinger equation of the type.

\[ H \Psi_i = \{T + V_i(\vec{r})\} \Psi_i = E_i \Psi_i \]  \hspace{1cm} (2.38)

Here \( E_i \) is the energy of ith state while \( T \) is the kinetic energy operator \( \left(-\frac{\hbar^2}{2m} \nabla^2\right) \)

\( V_i(\vec{r}) \) 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 energied \( E_k \). 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 band of simple metals allows the
effect of periodic potential on the electrons to be treated as perturbation. In the
small core approximation the core states are the same 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.

$$H|\Psi_k \rangle = (\Gamma + V_{\text{f}}(\vec{r}'))|\Psi_k \rangle = E_k |\Psi_k \rangle \quad (2.39)$$

If the wave function is expanded by choosing the plane waves then large number of plane waves are needed to get reasonably correct wave function. According to Herring [11] and 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

$$\text{OPW}_k = e^{iK \vec{r}} - \sum_{\alpha} \psi_\alpha (\vec{r}) \psi_\alpha^* (\vec{r}') e^{iK \vec{r}} d\tau \quad (2.40)$$

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

$$|K\rangle = \Omega^{-\frac{1}{2}} e^{iK \vec{r}} \quad (2.41)$$

$$|\alpha \rangle = \psi_\alpha (\vec{r}) \quad (2.42)$$

35
In which $|\tilde{K}>$ denotes the plane waves and $|\tilde{a}>$ is the core wave functions. The normalized plane waves in this notation become as

$$\text{OPW}_K = |\tilde{K}> - \sum_{\alpha} |\alpha> <\alpha|\tilde{K}>$$  \hspace{1cm} (2.43)

Where a bra $<\alpha| = |\alpha>^*$ and a ket facing each other represent an integral:

$$<\alpha|\tilde{K}> = \Omega^{-1/2} \int \psi^*_\alpha(r) e^{ikr} \, dr$$  \hspace{1cm} (2.44)

Some times it is very useful to write OPW in terms a projection operator $P$ which projects any wave function on to the core state so we write

$$P = \sum_{\alpha} |\alpha><\alpha|$$  \hspace{1cm} (2.45)

So OPW takes the form

$$\text{OPW}_K = (1-P)|\tilde{K}>$$  \hspace{1cm} (2.46)

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

$$\psi_k = \sum_q C_q (\tilde{K})(1-P)|\tilde{K} + \tilde{q}>$$

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

$$\sum_q C_q (\tilde{K}) H(1-P)|\tilde{K} + \tilde{q}> = E_k \sum_q C_q (\tilde{K})(1-P)|\tilde{K} + q>$$  \hspace{1cm} (2.48)

Multiplying on left by $<\tilde{K} + \tilde{q}|$ keeping in view that
\[ HP = \sum_{\alpha} E_{\alpha} |\alpha > \alpha| \text{ we get} \]

\[ C_q(\vec{K}) = \frac{\hbar^2}{2m} |\vec{K} + \vec{q}|^2 + \sum_{q} C_q(\vec{K}) \{ <\vec{K} + \vec{q}|V|\vec{K} + \vec{q}> \]

\[ - \sum_{\alpha} E_{\alpha} <\vec{K} + \vec{q}|\alpha > \vec{K} + \vec{q}> \]

\[ = [C_q(\vec{K}) - \sum_{q} C_q(\vec{K}) <\vec{K} + \vec{q}|P|\vec{K} + \vec{q}> ]E_k \]

This is called orthogonalized plane wave (OPW) calculation.

2.7 THE PSEUDOPOTENTIAL AND CANCELLATION THEOREM:

It was noted by Phillips and Kleiman [10] that all the terms in the projection operator in equation (2.48) 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

\[ W = V(\vec{r}) + \sum_{\alpha} (E_k - E)|\alpha > \alpha| = V(\vec{r}) + E_k - H \]

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

\[ \varphi_k = \sum_{q} C_q(\vec{K}) |\vec{K} + \vec{q}> \]

where \( C_0(\vec{K}) = 1 \)

The equation (2.50) 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 $V_1(\vec{r})$, a local potential that depends only on position $(\vec{r})$. 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 $V_1(\vec{r})$ is attractive. The second term in the pseudopotential equation (2.51) contains the difference $(E_k - E_u)$ which will always be positive since the core energies $E_u$ lie below $E_k$. The projection operator $P$ is essentially positive and therefore, this positive term will cancel to some extent the attractive potential $V_1(\vec{r})$. 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.

2.8 ELASTIC 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 vibration 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 \( \mathbf{q} \to 0 \) the well known Christoffel equation for solids is

\[
[D(\mathbf{q}) - \omega^2 \mathbf{I}] u(\mathbf{K}) = 0
\]

\[
\text{Lim } q \to 0 \left| \mathbf{C}_{\alpha\beta\delta\xi} q_{\gamma} q_{\delta} - \mathbf{P} \mathbf{W}^2 \delta_{\alpha\xi} \right| = 0
\]

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

\[
\begin{align*}
C_{1111} &= C_{2222} = C_{11}, C_{3333} = C_{33} \\
C_{1212} &= C_{66} = 1/2 (C_{11} - C_{12}); C_{1313} = C_{2323} = C_{44}
\end{align*}
\]

39
and \[ C_{1133} = C_{13} \] (2.54)

The solution of equation (2.53) along the high symmetry directions are simple and for direction [0001] it gives

\[ \text{Lim } q \to 0 \frac{p w^2}{q^2} = C_{33} \text{ for LA mode} \]

\[ \text{Lim } q \to 0 \frac{p w^2}{q^2} = C_{44} \text{ for TA mode} \]

The solution is symmetry direction [01\overline{1}0] gives.

\[ \text{Lim } q \to 0 \frac{p w^2}{q^2} = \leftarrow C_{11} \text{ for LA mode} \]

\[ \text{Lim } q \to 0 \frac{p w^2}{q^2} = \leftarrow C_{44} \text{ for } TA_\perp \text{ mode} \] (2.55)

\[ \text{Lim } q \to 0 \frac{p w^2}{q^2} = \leftarrow \frac{1}{2} (C_{11} - C_{12}) \text{ for } TA_{11} \text{ mode.} \]

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 [13].

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 [01\overline{1}0] symmetry directions which become identical in the light of rotational invariance condition of the crystal.
2.9 CRYSTAL EQUILIBRIUM CONDITIONS:

The real crystal 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 lattice 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 fulfillment 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.

\[ (i) \sum_{l,k} V(l', kk')X_{\alpha}(l', kk') = 0 \]  \hspace{1cm} (2.56)

\[ (ii) \sum_{k,k'} V(l', kk')X_{\alpha}(l', kk')X_{\beta}(l', k'k) = 0 \]  \hspace{1cm} (2.57)
Where \( V(l', k') \) denotes the first order space derivative of potential between two atoms situate at positions \((l'k')\) and \((ok)\) respectively, \(X_{n}(ok, l'k')\)

Denotes the relative coordinates of atom \((l'k')\) with respect to the atom at the origin.

If we sum the terms of left hand side of equations for each value of \(k\) only \((r-1)\) are independent, and hence equation (2.57) represent a set of \(3(r-1)\) mutually independent equations (where \(r\) denotes the number of atoms per unit cell).

Further equation (2.57) symmetric in Cartesian indices \(\alpha\) and \(\beta\), 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.

**2.10 HUANG'S COMPATIBILITY CONDITIONS:**

The set of equilibrium conditions (2.56) and (2.57) 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 \((q \to 0)\). In long wave length limit acoustic vibration of the lattice represent elastic waves in the solid. This not only introduces elastic constant 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 condition for stress to vanish. Huang [14] 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 $\alpha, \beta, \gamma, \lambda = 1, 2, 3$.

\[
[a\beta, y, \lambda] = [a\beta, \lambda y] = [\beta\alpha, y, \lambda] = [\beta\alpha, \lambda, y]
\] (2.58)

with symbols and brackets having their usual meaning. In content of the central pairwise potential, the equilibrium conditions (2.55) becomes,

\[
V_0 (k) = 2 \sum_{l,k} V_l (X_{\alpha}) |_{x (r, kk')} = 0
\] (2.59)

While the equilibrium condition (i) now becomes,

\[
\sum_{l,k} [V' (X_{\alpha} X_{\beta})] |_{x (k, ll')} = 0
\] (2.60)

which is identical to equilibrium condition (2.57) 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.

2.11 EQUILIBRIUM CONDITION FOR HCP STRUCTURE:

A detailed description of hcp structure has been given in chapter 1.

The two atoms of type $k = 1$ and $k = 2$ belonging to unit cell are situated at position $(0,0,0)$ and $(0, \frac{\sqrt{3}}{2} a, \frac{c}{2})$ respectively with respect to the atom of type $k = 1$ at origin, the distance of various neighbours are as follows
If we designate the number of neighbour 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 \( \alpha \neq \beta \) (two of equilibrium conditions (2.60) and (2.61) are automatically satisfied, while for \( \alpha = \beta \) relations (1.62) and (1.63) lead to the following equilibrium conditions

\[
\sum_j \sum_{jth \text{ neighbour}} [V^1(x_j^2)]_{x(j)} = \sum_j \sum_{jth \text{ neighbour}} [V^1(x_j^2)]_{x(j)} - 0
\]

and

\[
\sum_j \sum_{jth \text{ neighbour}} [V^1(x_j^2)]_{x(j)} = 0
\]  \hspace{1cm} (2.60)

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

\[
V^1_1(r_1) + 3 V^1_2(r_2) + 4 V^1_3(r_3) = 0 \]  \hspace{1cm} (2.61)

and

\[
V^1_1(n) + V^1_3(r_3) = 0 \]  \hspace{1cm} (2.62)

These equilibrium conditions for hcp structure can equivalently be written as

\[
\begin{bmatrix}
\left( \frac{\partial V}{\partial a} \right)_c = 0 \\
\left( \frac{\partial V}{\partial c} \right)_a = 0 
\end{bmatrix}
\]  \hspace{1cm} (2.63)

Where

\[
V = \frac{1}{2} |6 V^1_1(r_1) + 6 V^2_2(r_2) + 6 V^3_3(r_3)|
\]
Is the total interaction potential per ion. The conditions (2.64) and (2.65) 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

\[
\sum_j \sum_{\text{jth neighbour}} [V x^2_j]_{x(j)} = \sum_j \sum_{\text{jth neighbour}} [V x^2_j]_{x(j)}
\]

(2.64)

Which is equivalent to

\[
\left( \frac{\partial V}{\partial \alpha} \right)_c = \left( \frac{\partial V}{\partial \epsilon} \right)_a
\]

(2.65)

Thus in equilibrium an hcp lattice, force of external stress, must satisfy the condition (2.61) and (2.62) and (2.65). In such a case, for hcp system relation (2.57) gives

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

Which means that the two expressions of \( C_{44} \) obtained from [0001] and [0101] are identical in view of condition (2.67).
REFERENCES


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46