### FORMALISM AND COMPUTATIONAL DETAILS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Introduction</td>
<td>15</td>
</tr>
<tr>
<td>2.2 Formalism</td>
<td>15</td>
</tr>
<tr>
<td>2.2.1 LCGO method</td>
<td>15</td>
</tr>
<tr>
<td>2.2.1.1 Overview of the Formalism</td>
<td>22</td>
</tr>
<tr>
<td>2.2.2 Self consistent procedure</td>
<td>32</td>
</tr>
<tr>
<td>2.2.3 Momentum distribution of electrons</td>
<td>37</td>
</tr>
<tr>
<td>2.3 Computational Details</td>
<td>42</td>
</tr>
<tr>
<td>2.3.1 Choice of Basis function</td>
<td>42</td>
</tr>
<tr>
<td>2.3.2 Fourier Coefficient of Crystal potential (FCOF)</td>
<td>42</td>
</tr>
<tr>
<td>2.3.3 Hamiltonian and overlap Integrals (ESINT)</td>
<td>47</td>
</tr>
<tr>
<td>2.3.4 Matrix Elements</td>
<td>52</td>
</tr>
<tr>
<td>2.3.5 Generalised overlap Integrals</td>
<td>55</td>
</tr>
<tr>
<td>2.3.6 Self Consistency (SCF1 or SCF2)</td>
<td>56</td>
</tr>
<tr>
<td>2.3.7 Final band structure</td>
<td>59</td>
</tr>
</tbody>
</table>
2.1 INTRODUCTION

This chapter is divided into two parts viz. Formalism and computational details. Some of definitions given in Chapter 1 are not stated in this chapter to avoid repetition. In section 2.2 the formalism required for the calculation of the properties mentioned in the present work are presented. The details of the LCGO formalism have been extracted from the work of Wang and Callaway [78].

In section 2.3 the details of the calculations are presented. Details of the band package (BNDPKG) developed by Callaway and co-workers for the calculation of self-consistent LCGO method are described.

2.2 FORMALISM

2.2.1 LCGO Method

A band structure method solves the single particle wave equation (2.1) (in atomic units). If wave function $\psi_n$ refers to a state of wavevector $k$ in band $n$, depending on the context, the band index will also include the spin direction. $\psi_n$ will be called the Bloch function as it obeys the Bloch's theorem

$$[-\nabla^2 + V(r)]\psi_n(k,r) = E_n(k)\psi_n(k,r) \quad \ldots \quad (2.1)$$

$$\psi_n(k,r + R_p) = \exp(ik \cdot R_p)\psi_n(k,r) \quad \ldots \quad (2.2)$$

in which $R_p$ is any direct lattice vector. The energy band is described by the band function $E_n(k)$. The potential $V(r)$ contains two terms:

Chapter 2

1. The coulomb potential of the (fixed) nuclei and of the average distribution of the electrons in the system.

2. An exchange correlation potential as represented in the local density approximation with allowance for possible spin polarization.

\[ V_{\text{xc}}(r) = 2Z \sum_{\mu} \frac{1}{|\mathbf{r} - \mathbf{r}'|} + 2 \int \frac{\rho_\sigma(r)}{|\mathbf{r} - \mathbf{r}'|} d^3r + V_{\text{xc}} \]  \( \text{(2.3)} \)

In the above equation, \( Z \) is the atomic number of a nucleus, \( V_{\text{xc}} \) is the spin-polarised form of the exchange-correlation potential introduced by Von Barth and Hedin (VBH)\( [74] \) and is given by

\[ V_{\text{xc}} = A(\rho) \left( \frac{2\rho_\sigma}{\rho} \right)^{1/3} + B(\rho) \]  \( \text{(2.4)} \)

where \( \rho_\sigma \) is the charge density of electrons of spin \( \sigma \)

\[ \rho_\sigma(r) = \sum_{k,n,s} \delta_{\sigma,s} \theta[E_F - E_n(k)] |\psi(k,r)|^2 \]  \( \text{(2.5)} \)

(in which \( \theta \) is a unit step function: \( \theta(x) = 1 \) if \( x \geq 0 \), \( \theta(x) = 0 \) if \( x < 0 \), and \( E_F \) is the Fermi energy); \( \rho \) is the total charge density \( \rho(r) = \Sigma \rho_\sigma(r) \)

It is assumed that the lattice is cubic FCC and that there is only one atom per unit cell. Suppose that the charge densities are fixed, then (2.1) becomes a linear equation, and it is solved by an expansion method in which the Bloch function is expanded in a set of chosen basis functions \( \phi_i(k,r) \) which themselves satisfy Bloch theorem

\[ \psi(k,r) = \Sigma_{i} C_{ri}(k) \phi_i(k,r) \]  \( \text{(2.6)} \)

in which \( C_{ri} \)'s are the coefficients to be determined. The \( \phi_i \) are constructed as properly phased LCGO's \( u_i \) placed on the lattice sites of the system:

\[ \phi(k,r) = (N)^{1/2} \sum_{\mu} \exp(ik \cdot R_{\mu}) u_{\mu}(r-R_{\mu}) \]

in which \( N \) is the number of atomic cells in the (large) crystal volume. The individual orbitals \( u_{\mu} \) have the form,

\[ u_{\mu}(r) = N_{\mu} r^{l_{\mu}} \exp(-\alpha_{\mu} r^{2}) K_{l_{\mu}j_{\mu}}(r) \]

in which \( N_{\mu} \) is a normalisation constant.

\[ N_{\mu} = \left( \frac{2(2\alpha_{\mu})^{l_{\mu}+3/2}}{\Gamma(l_{\mu}+3/2)} \right)^{1/2} \]

... (2.9)

The angular function \( K_{l_{\mu}j_{\mu}}(r) \) is given as cubic harmonic [79] of order \( l_{\mu} \), type \( j_{\mu} \), normalized to unity with respect to integration over solid angles.

Using Equation (2.9) in (2.1), followed by projection on an arbitrary \( \phi_{j_{\mu}}(k,r) \), leads to the matrix equation

\[ \Sigma H_{j_{\mu}}(k) C_{n}(k) = E_{n}(k) \Sigma S_{j_{\mu}}(k) C_{n}(k) \]

... (2.10)

in which the Hamiltonian and overlap matrices are given by [80]

\[ H_{j_{\mu}}(k) = \Sigma \exp(-ik \cdot R_{\mu}) E_{j_{\mu}}(R_{\mu}) \]

... (2.11a)

\[ S_{j_{\mu}}(k) = \Sigma \exp(-ik \cdot R_{\mu}) S_{j_{\mu}}(R_{\mu}) \]

... (2.11b)
The matrix elements of the Hamiltonian are separated into kinetic energy \( (T) \) and potential energy \( (V) \) contributions,

\[
E_q(R) = \int u^*_q(r-R) H u_q(r) \, dr 
\]  
\[
S_q(R) = \int u^*_q(r-R) u_q(r) \, dr 
\]

The overlap integrals can be readily evaluated using the Gaussian basis. The kinetic energy integrals \( T \) are found by differentiation of the overlap integrals. The evaluation of potential energy integrals is facilitated by the use of a Fourier representation of the crystal potential \[1,81\].

\[
V(r) = \sum_k V(k) \cos(k \cdot r) 
\]

in which \( k \) is a reciprocal lattice vector (RLV) and \( V(k) \) is the Fourier coefficient of potential. Thus,

\[
V_q(R) = \sum_k V(k) \int u^*_q(r-R) \cos(k \cdot r) u_q(r) \, dr 
\]

The use of Gaussian orbitals permits analytic evaluation \[82\] of the integrals which occur in (2.15). The convergence of the sum over reciprocal lattice vectors (RLV’s) may be slow, due to the contribution of the nuclear terms as well as the screening potential due to lightly bound electrons. An Ewald type procedure is used to get quick convergence. A potential \( v \) is added to and subtracted from the Coulomb potential in each cell.
\[ V_c(\mathbf{r}) = [V_1(\mathbf{r}) - V(I)] + V_i(\mathbf{r}) \] \hspace{1cm} \text{(2.16)}

such that \( V_c - V_1 \) is reasonably slowly varying near the nucleus. But \( V_1 \) is of sufficiently short range so that matrix elements of \( V_i(\mathbf{r}) \) can be evaluated directly "in real space" without consideration of three centre integrals. \( V_i(\mathbf{r}) \) has been chosen to be of the form

\[ V_i(\mathbf{r}) = \sum_{\alpha} V_{\alpha}(r-R_{\alpha}) \] \hspace{1cm} \text{in which,}

\[ V_{\alpha}(r) = \frac{2Z}{r} \exp(-\beta_1 r^2) \left( \frac{\alpha}{r} \{\exp(-\beta_1 r^2) - \exp(-\beta_2 r^2)\} \right) \] \hspace{1cm} \text{(2.17)}

The constants \( \alpha, \beta_1, \beta_2 \) are chosen empirically. A self-consistent band calculation involves an iterative process in which, the energy levels and wave functions from one stage of the calculation are used to compute a revised crystal potential for use in the next stage. Fortunately, given a reasonable starting potential, it suffices to consider changes in a reasonably small number of Fourier co-efficients \( V(K) \) (typically 20 to 50 independent \( V \) values). Different procedures have to be used for the changes in the Coulomb and in the exchange-correlation potentials. Let us consider the Coulomb potential first. Since Poisson's equation is linear, one can relate a change in the density of electrons, \( \delta \rho \) to a change \( \delta V \) in the potential by

\[ \nabla^2 \delta V(\mathbf{r}) = -8\pi \delta \rho(\mathbf{r}) \]

The corresponding changes in the Fourier co-efficients are connected by

\[ \delta V(K) = \frac{8\pi \delta \rho(K)}{(K^2)} \] \hspace{1cm} \text{(2.19)}
in which $\delta \rho(K_s)$ is the change in Fourier co-efficient of the electron density. The change in $\rho(r)$ with respect to the initially assumed function $\rho_0$ is

$$\delta \rho(r) = \left[ \sum_{i} \sum_{\mathbf{k}} C_{ai}^{*}(\mathbf{k}) C_{aj}(\mathbf{k}) \phi_{i}^{*}(\mathbf{k},x) \phi_{j}(\mathbf{k},x) \right] - \rho_0(r) \quad \text{...(2.20)}$$

in which $n$ and $k$ summation refers to states occupied in the current iteration. The Fourier co-efficients of $\delta \rho$ are

$$\delta \rho(K_s) = (N\Omega)^{1/3} \sum_{i} \sum_{\mathbf{k}} C_{ai}^{*}(\mathbf{k}) C_{aj}(\mathbf{k}) S_{ij}(\mathbf{k},K_s) - \rho_0(K_s) \quad \text{...(2.21)}$$

in which $\rho_0(K_s)$ are the Fourier co-efficients of $\rho_0(r)$, $\Omega$ is the volume of the unit cell, and the $S_{ij}(\mathbf{k},K_s)$ are generalised overlap integrals:

$$S_{ij}(\mathbf{k},K_s) = \Sigma \exp(-i\mathbf{k} \cdot \mathbf{R}_u) \int u_{i}^{*}(\mathbf{r} - \mathbf{R}_u) \exp(-i\mathbf{k} \cdot \mathbf{r}) u_{j}(\mathbf{r}) d^{3}\mathbf{r} \quad \text{...(2.22)}$$

It is also noted that

$$N^{-1} \sum_{k}^{\infty} \left[ \frac{\Omega}{(2\pi)^{3}} \right] \int d^{3}k$$

The $k$ integral runs over the Brillouin zone (BZ). A single computation of the generalised overlap integrals suffices for all the iteration of a self-consistent calculation. Equation (2.19) fails for $K_s=0$. However, a separate formula is used to cover this case.

The computation of the change in the Fourier co-efficient of the exchange-correlation potential contained in (2.3) is more difficult, because of the presence of the cube root of the charge density. In this case it is necessary to assume that $\delta \rho(r)$ is sufficiently small compared to $\rho_0(r)$ so that one can adequately approximate the cube root as

$$\rho^{1/3}(r) = (\rho_0 + \delta \rho)^{1/3} \approx \rho_0^{1/3}(r) + \frac{1}{3} \frac{\delta \rho(r)}{\rho_0^{2/3}(r)} \quad \text{...(2.24)}$$

The $\delta \rho$ used in the calculation of exchange-correlation potential is the difference between the current and the starting (zeroth iteration) charge density. In order to use (2.24), one has to compute the Fourier co-efficients of $\rho_0^{-2/3}(r)$ which is given by

$$p_{m}(K) = (\Omega)^{-1} \int \exp(-ik \cdot r)[\rho_0(r)]^{2/3}d^3r$$

...(2.25)

The integral runs over a single unit cell. The computation is not difficult and $p_{2/3}(K_s)$ tends to decrease rapidly with increasing $|K_s|$.
2.2.1.1 Overview of the Formalism

The spherical averaged total charge density for electrons of spin $\sigma$ can be written as

$$\rho_\sigma(r) = \frac{1}{|R_\sigma|} \sum_{R_\sigma} \rho_{\sigma_0}(r - R_\sigma)$$

Where $\rho_\sigma(r)$ is the atomic charge density. The summation from each lattice site was carried out up to the shell of neighbours where the desired degree of convergence has been reached. Although the individual atomic charge densities were assumed to be spherically symmetric, the superposed density has only cubic symmetry about any lattice site. The above bracket $<...>_{av}$ stands for the spherical average evaluated in the following way: The total charge density is expanded in a series of Kubic harmonics up to the eighth order. The spherical average $\rho_\sigma(r)$ is approximated as the zeroth order term in the expansion, and can be obtained by solving a set of four linear inhomogeneous equations along four inequivalent directions. Finally, the 96 point Gaussian formula was used to perform the numerical integration in the Wigner-Seitz sphere for each given reciprocal lattice vectors.

The one electron Schrödinger equation to be solved takes following form

$$H\psi_n(K,r) = E_n(k)\psi_n(K,r)$$

where $H$ is the Hamiltonian. The crystal function $\psi_n(K,r)$ were expanded as a series in the basis function

$$\psi_n(K,r) = \sum_i a_n(k) \phi_i(K,r)$$
in which \( n \) is the band index and \( K \) is the wave vector of the state. The set of basis functions consisting of only atomic states does not form a complete set, so the corresponding eigenfunctions are not the exact solution of the Schrödinger equation. However inclusion of all the bound states and some of the excited states can be expected to yield a fair approximation to the actual wavefunctions. The expansion coefficient \( a_n(k) \) and energy \( E_n(k) \) are to be determined by solving the Secular equation

\[
\text{Det} | H_{mn}(K) - S_{mn}(K) | = 0 \quad \text{(2.26c)}
\]

where

\[
H_{mn}(K) = \langle \phi_m(K, \mathbf{r}) | H | \phi_n(K, \mathbf{r}) \rangle
\]

\[
= \sum \exp(-ik \cdot R_p) \int u_m^*(\mathbf{r}-\mathbf{R}_p) H u_n(\mathbf{r}) \, d^3r
\]

\[
= T_{mn}(K) + V_{mn}(K) \quad \text{(2.27)}
\]

The kinetic energy matrix is given by

\[
T_{mn}(K) = \sum \exp(-ik \cdot R_p) \int u_m^*(\mathbf{r}-\mathbf{R}_p) (-\nabla^2) u_n(\mathbf{r}) \, d^3r \quad \text{(2.27a)}
\]

The matrix element of the crystal potential expanded in fourier series over the reciprocal lattice vectors can be expressed as follows
The generalized overlap matrix is given by

\[ S_{\alpha\mu}(K,\nu) = \sum_{R_p} e^{ik_{s}R_p} \int_{-\infty}^{\infty} u_{\alpha}^{*}(r-R_p) e^{ik_{s}r} u_{\nu}(r) \, dr \]  

(2.27c)

For a crystal with inversion symmetry the \( e^{ik_{s}r} \) term in the above equation can be replaced by \( \cos(K_{s}r) \). The overlap matrix element in eq. (2.26c) is

\[ S_{\alpha\mu}(K) = S_{\alpha\mu}(K,0) \]  

(2.27d)

All these matrix elements can be evaluated analytically provided one choose linear combinations of Gaussian type orbitals (GTO) as the basis functions.

No method has yet been found to express them in a closed form when the atomic wave functions are expanded in Slater-type orbitals. This was the reason for choosing GTO in the expansion of the basis function. We shall evaluate the integral

\[ < u_{l,m,n}(r_A) | \cos(K_{s}r) | u_{q,s,t}(r_B) > \]

following the procedure modified by Chaney and Dorman [83].

The function \( u_{l,m,n}(r) \) are GTO of order \((l,m,n)\)

\[ u_{l,m,n}(r) = X^{\alpha_{1}}Y^{\alpha_{2}}Z^{\alpha_{3}} e^{\alpha_{1}r} \]  

(2.27e)

Appropriate normalization constants for both the orbital and the angular parts of the wave functions have to be included. The orbital on the left hand side has exponent \( \alpha_{1} \) and is centered at the lattice site A and that on the right side has exponent \( \alpha_{2} \) and is centered at B as shown in Fig. 2.1.
Figure 2.1 Co-ordinates for the evaluation of three central integrals.
The integral appearing in eq. (2.27c) can be obtained by putting B and C at the origin.

\[ \langle u_{lmn}(r_A) | \cos Kr_C | u_{qmn}(r_B) \rangle \]

\[ = \int d^3r_A Y^m_A Z^n_A \exp(-\alpha_1 r_A^2) \cos Kr_C Y^q_r Z^q_r \exp(-\alpha_2 r_B^2) \ldots (2.27f) \]

where

\[ r_A = r - A, \quad r_B = r - B, \quad r_C = r - C \]

The product of two Gaussians situated at center A and B is proportional to a third Gaussian situated at a point D along the line AB.

\[ \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) = \exp\left[ -\frac{\alpha_1 + \alpha_2}{AB^2} r_D^2 \right] \exp\left[ -\left( \alpha_1 + \alpha_2 \right) r_D^2 \right] \ldots (2.27g) \]

\[ r_D = \frac{\alpha_1 A + \alpha_2 B}{\alpha_1 + \alpha_2} \quad \text{and} \quad AB = B - A \ldots (2.27h) \]

Writing

\[ r_A = r_D + AD, r_B = r_D + BD \quad \text{and} \quad r_C = r_D + CD \ldots (2.28) \]

and taking the binomial expansion, the integral can be written as
\[
\xi \Sigma ( ) ( ) ( ) ( ) ( ) ( ) (AD)_x^{1a}(AD)_y^{m-b}(AD)_z^{n-c}
\]
\[
\text{abc a b c d e f}
\]
\[
\text{def}
\]
\[
(BD)_x^{e-d}(BD)_y^{s-e}(BD)_z^{t-f}
\]
\[
[\cos K \cdot CD <u_{a,b,c}(r_D)|\cos K_x r_D|u_{a,s,e}(r_D)>]
\]
\[
-sin K \cdot CD <u_{a,b,c}(r_D)|\sin K_x r_D|u_{a,s,e}(r_D)>
\]
\[
...(2.28a)
\]
where
\[
\xi = \exp \left[ - \frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \Delta R^2 \right]
\]
\[
...(2.28b)
\]
and ( ) are binomial coefficients with 0 \leq a \leq 1. The remaining integrals are central cell integrals about lattice site \(D\). These can be evaluated analytically in Cartesian coordinates. For a crystal with inversion symmetry only those terms which are even functions of \(K_x, K_y, K_z\) will contribute. The integrals can be reduced to

\[
\xi \Sigma ( ) ( ) ( ) ( ) ( ) ( ) (AD)_x^{1a}(AD)_y^{m-b}(AD)_z^{n-c}
\]
\[
\text{abc a b c d e f}
\]
\[
\text{def}
\]
\[
(BD)_x^{e-d}(BD)_y^{s-e}(BD)_z^{t-f}
\]
\[
(-1)^{a+b+c+d+e+f} G_{a,b,c}(K_x, CD_x) G_{b,c,e}(K_y, CD_y) G_{c,e,f}(K_z, CD_y) \quad ...(2.28c)
\]
In this case that \(n\) is an even number

\[
G_n(K, R) = \frac{(-1)^{a_2}}{2^n} (\pi \gamma)^{1/2} \exp \left( - \frac{\gamma K^2}{4} \right) H_n(-, \gamma) \cos(KR)
\]
\[
...(2.28d)
\]
\[ \gamma = \frac{1}{\alpha_1 + \alpha_2} \]  

...(2.28e)

\( H_n(\frac{-\gamma}{2}, \gamma) \) is a Hermite polynomial satisfying the following recurrence relation

\[ H_{n+2} \left( \frac{-\gamma}{2}, \gamma \right) = K \gamma H_{n+1} \left( \frac{-\gamma}{2}, \gamma \right) - 2(n+1)\gamma H_n \left( \frac{-\gamma}{2}, \gamma \right) \]  

...(2.28f)

\[ H_0 \left( \frac{-\gamma}{2}, \gamma \right) = 1 \] and

\[ H_1 \left( \frac{-\gamma}{2}, \gamma \right) = K \gamma \]  

...(2.28g)

in the case in which \( n \) is an odd number,

\[ G_n(K, \gamma) = K \Gamma \left( \frac{-\gamma}{2} + 1 \right) \gamma^{n/2} \frac{3}{2} K^{-3} F_1 \left( \frac{-\gamma}{2}, \frac{-\gamma}{2}, \frac{-\gamma}{2}, \frac{-\gamma}{2} \right) \]  

...(2.28h)

where \( \Gamma \left( \frac{-\gamma}{2} + 1 \right) \) is the Gamma function and,

\[ \frac{n}{2} \gamma K^2 \frac{3}{2} \]  

\( F_1 \left( \frac{-\gamma}{2}, \frac{-\gamma}{2}, \frac{-\gamma}{2}, \frac{-\gamma}{2} \right) \) is a confluent hypergeometric function

satisfying the following relation

\[ F_1 \left( \frac{-\gamma}{2}, \frac{-\gamma}{2}, \frac{-\gamma}{2}, \frac{-\gamma}{2} \right) + \frac{n}{2} \gamma K^2 \frac{3}{2} F_1 \left( \frac{-\gamma}{2}, \frac{-\gamma}{2}, \frac{-\gamma}{2}, \frac{-\gamma}{2} \right) = 0 \]  

...(2.28i)
with
\[ F_1\left(\frac{3}{2}, \frac{3}{2}; X\right) = e^X \quad \text{and} \quad F_1\left(\frac{5}{2}, \frac{3}{2}; X\right) = (1+3/2)e^X \].

The overlap matrix elements can easily be obtained by setting \( k = 0 \). The gradient kinetic energy matrix elements can be expressed as linear combinations of overlap matrix elements in the following way

\[ \langle u_\ell m \left| \nabla \times \right| u_{\alpha \beta} \rangle = q \langle u_\ell m \left| u_{\alpha \beta} \right\rangle - 2\alpha \left( q \right) < u_\ell m \left| u_{\alpha \beta} \rangle \rangle - 4 \alpha^2 \left| u_\ell m \left| u_{\alpha \beta} \rangle \rangle \right. \]

\[ \langle u_\ell m \left| \nabla \times \right| u_{\alpha \beta} \rangle = q \langle u_\ell m \left| u_{\alpha \beta} \rangle \rangle + 2\alpha \left( q \right) < u_\ell m \left| u_{\alpha \beta} \rangle \rangle - 4 \alpha^2 \left| u_\ell m \left| u_{\alpha \beta} \rangle \rangle \right. \]

Similar expression can be obtained for the Y and Z components. The Hamiltonian and overlap matrix elements are either real or imaginary depending on the parity of the wavefunction. We label them as follows

\[ H = \sum_{\ell m} \left| u_\ell m \rangle \langle u_\ell m \left| \right. \right. \]

\[ I_{nm} = \langle u_{n}\left( r - R_p \right) \right| H \left| u_{m}\left( r \right) \rangle \rangle \]

consider the unitary transformation $H' = U H U^{-1}$ with

$$ U = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{...(2.30c)} $$

The result is

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<th>d</th>
<th>s</th>
<th>p</th>
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<tr>
<td>d</td>
<td>$I_d \cos(K \cdot R_p)$</td>
<td>$I_s \cos(K \cdot R_p)$</td>
<td>$I_p \sin(K \cdot R_p)$</td>
</tr>
<tr>
<td>s</td>
<td>$I_s \cos(K \cdot R_p)$</td>
<td>$I_s \cos(K \cdot R_p)$</td>
<td>$I_p \sin(K \cdot R_p)$</td>
</tr>
<tr>
<td>p</td>
<td>$I_p \sin(K \cdot R_p)$</td>
<td>$I_p \sin(K \cdot R_p)$</td>
<td>$I_p \cos(K \cdot R_p)$</td>
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H'=$\Sigma_{R_p}$

here $H'$ is real and symmetric but the pd and ps block must be evaluated with care to avoid a possible error of negative sign. The eigenvectors of the transformed secular equation are

$$ \alpha_{\alpha m}^{'}(K) = \sum_{\alpha m} U_{\alpha m} a_{\alpha m}(K) \quad \text{...(2.30e)} $$

The momentum matrix elements between the cell periodic part of the wavefunctions

$$ W_\alpha(K, \tau) = e^{iK \cdot \tau} \psi_\alpha(K, \tau) \quad \text{...(2.30f)} $$

(the crystal momentum representation) are defined as $P_{\alpha \alpha m}(K) = M_{\alpha \alpha m}(K) + \hbar K \delta_{\alpha m}$ in which the momentum matrix elements between the crystal wavefunctions $M_{\alpha \alpha m}(K)$ can be evaluated in a similar way.

\[ M_{mn}(K) = \sum_{lj} a_{l}^{*}(K) P_{lj}(K) a_{mj}(K) \]

\[ = \sum_{lj} (U^{-1} a^{*}(K))_{l}^{*} P_{lj}(K) (U^{-1} a^{*}(K))_{mj} \]

\[ = \sum_{lj} a_{l}^{*}(K) P_{lj}(K) U U^{-1} a_{n}^{*}(K) \]

where,

\[
\begin{pmatrix}
    d \\
    s \\
    p
\end{pmatrix}
\begin{pmatrix}
    -\nabla_d \sin(K \cdot R_p) & -\nabla_s \sin(K \cdot R_p) & i \nabla_p \cos(K \cdot R_p) \\
    -\nabla_d \sin(K \cdot R_p) & -\nabla_s \sin(K \cdot R_p) & i \nabla_p \cos(K \cdot R_p) \\
    -i\nabla_p \cos(K \cdot R_p) & -i \nabla_s \cos(K \cdot R_p) & -\nabla_p \sin(K \cdot R_p)
\end{pmatrix}
\]

...(2.30g)

The gradient matrix elements

\[ \nabla_{mn} = \langle u_n(r-R_p) | \nabla | u_m(r) \rangle \]

...(2.30i)

are given in eq. (2.29) In the following section we shall discuss the selfconsistent procedure and the choice of the exchange parameter \( \alpha \).

2.2.2 Self consistent procedure.

In this section we shall outline the essential feature of the self-consistency procedure [84].

This is accomplished by an iterative method. At any given iteration a potential was constructed from the band wave functions calculated in the previous iteration. The new potential was again used to calculate a new set of wave functions. The procedure was repeated until the desired degree of convergence was achieved. The fundamental problem is to determine a new (or iterated) potential after a given stage of band structure has been completed. Since the calculation requires only the Fourier co-efficients of the potential it suffices to obtain these. It was observed that only the Fourier co-efficients of the potential for a few of the shortest reciprocal lattice vectors need to be considered in the iterative procedure to achieve self-consistency.

Higher co-efficients describe the charge density deep inside the core of an atom and do not change appreciably. For \( K_s = 0 \), the Fourier coefficients of the Coulomb potential can be expressed as [85].

\[
V(K_s) = \frac{-8\pi Z}{\Omega K^2} + \frac{\rho(K_s)}{K^2},
\]

...(2.31)

The Fourier coefficients of the electron density are given by

\[
\rho(K_s) = \frac{1}{N\Omega} \int \rho(\mathbf{r}) e^{-ik_s \cdot \mathbf{r}} d^3r
\]

in which the charge density can be written as

\[
\rho(\mathbf{r}) = \sum_{n\mathbf{K}} \left| \psi_n(K_s, \mathbf{r}) \right|^2
\]

...(2.32)

...(2.32a)

The Bloch function \( \psi_n(K_s, \mathbf{r}) \) are defined in Eq.(2.26b). The summation includes that portion of the Brillouin zone in which band \( n \) is occupied. Substituting Eq.(2.32a) into eq. (2.32) and converting the sum on \( K \) into an integral one obtains,
\[
\rho(K_s) = \frac{1}{(2\pi)^3} \sum_{n \text{ occupied}} \sum_{ij} d^3K a_i^*(K) S_{ij}(K,K_s)a_j(K) \tag{2.32b}
\]

The generalised overlap matrix \( S_{ij}(K,K_s) \) has been defined in eq. (2.27c). In the case \( K_s = 0 \) the Fourier coefficient of the Coulomb potential must be determined by a limiting process.

\[
V(0) = \lim_{K \to 0} \left[ -\frac{8\pi}{\Omega K^2} \frac{1}{K^2} \int e^{-ikr} \rho(r) d^3r \right] \tag{2.32c}
\]

This limit exists and can be obtained by expanding the exponential term in powers of \(|K|\) before taking the limit \( K \to 0 \). The result is

\[
V(0) = \frac{-4\pi}{3\Omega} \int \rho(r) r^2 d^3r \tag{2.32d}
\]

The integral is over the volume of the primitive cell. The charge in \( V(0) \) at a given stage of iteration can be evaluated analytically if we make the following assumptions: first, the integral over a primitive cell can be replaced by that over the Wigner-Seitz sphere, and second, the change in \( (K) \) is spherically symmetric. Thus we can write

\[
\Delta \rho(t) = \sum_{K_s} (|K_s|) e^{ik_s L} \tag{2.32e}
\]

Substituting eq. (2.32c) into eq. (2.32d) and evaluating the integral one obtains...

$$\Delta V(0) = \frac{-16\pi^2}{3\Omega} \sum_{K_s} \Delta \rho(|K_s|) \left[ \left( \frac{3r_0^2}{|K_s|^3} - \frac{6}{|K_s|^5} \right) \sin(|K_s|r_0) \right. + \left. \left( \frac{6r_0}{|K_s|} - \frac{r_0^3}{|K_s|^4} \right) \cos(|K_s|r_0) \right] \quad \ldots(2.32f)$$

where $r_0$ is the radius of the Wigner-Seitz sphere. The exchange potential presents more difficulty because of the cube root dependence on the charge density. It was evaluated in the following way. The change in the Fourier coefficients of charge density was averaged over directions of $K_s$ and the resulting Fourier series was summed to determine the change in charge density in an atomic cell.

The procedure just described has the disadvantage that the convergence in $\Delta \rho(K_s)$ is slower than that in $\Delta V_s(K_s)$ by an extra factor of $K_s^2$, and more terms in $\Delta V_s(V_s)$ have to be considered than necessary. An alternative procedure is to construct the iterated charge density directly from eq.(2.32a) and (2.26b).

This modification has been included in the self-consistency program. The changes in the coulomb and the exchange potential were added to the Hamiltonian matrix in the following way

$$H_{ij}(K) = H^0_{ij}(K) + \sum \left[ (\Delta V_s(K_s) + \omega\Delta V_s(K_s)) S_{ij}(K_s,K_s) \right] \quad \ldots(2.32g)$$

The $H_{ij}(K)$ was the iterated Hamiltonian while $H^0_{ij}(K)$ was the original Hamiltonian matrix defined in eq.(2.27). The new Hamiltonian was again diagonalized to obtain a new set of eigen values and eigen functions. This procedure was repeated until the desired degree of convergency has been achieved. At first the calculations employed by Wang and Callaway [78] on Ni a value of the exchange
parameter $\alpha$ close to unity ($\alpha = 0.972$), which had been found to give the most satisfactory results [86]. Where the charge density was sampled at 20 points in $1/48$ th of the Brillouin zone reasonably self-consistent results were obtained after about eight iterations. The resulting energy bands appeared to be unsatisfactory, both in regard to the relation of the p and d bands. Estimates were made by them which indicated that the exchange parameter $\alpha$ be decreased. Ultimately they used value of $\alpha = 2/3$ and the self consistent calculations were repeated with this value. The results obtained in this case were appeared to be in substantially better.

Another point of practical interest has to do with the number of iterations necessary to achieve convergence. In principle, when self consistency has been reached, the iterated potential $V_{out}(K_s)$ should be equal to the input potential $V_{in}(K_s)$ based on which $V_{out}(K_s)$ are evaluated. Therefore one should be free to modify the input potential at the beginning of each iteration by using

$$V_{in}'(K_s) = \beta V_{out}(K_s) + (1-\beta) V_{in}(K_s) \ldots (2.32h)$$

where the unprimed $V(K_s)$ are the iterated and input potentials for the last iteration. The weighting factor $\beta$ was allowed to vary between 0 and 1. Wang and Callaway [12] observed that the change in the Fourier coefficients of the Coulomb potential $V_c(K_s)$ oscillated rapidly about their final convergent values in the first few iterations. This was avoided choosing a value of $\beta$ which used to bring $V_c(K_s)$ closer to their convergent values. A value of $\beta$ close to 0.3 seemed to work very well for the first few iterations for transition metals. It was increased when the oscillations settle down, especially a change in $V_c(K)$ became monotonic.

The changes in the relative position of energy levels $L', L_2$ produced the additional problem. The change in the Fourier coefficients apparently became divergent after a rough degree of convergence seemed to have been achieved by them. This was caused by oscillations in the position of the $L_2$ with respect to the Fermi energy and which they were in a position to solve by introducing a very
small value of $\beta$. The criterion employed to define an adequate degree of self consistency by them was that the Fourier coefficients of Coulomb potential should be stable to 0.002 Ry. For the case $\alpha = 2/3$ eight iterations were made using 20 points in 1/48 th of the Brillouin zone followed by three iterations using 89 points. and they lateron predicted that it was sufficient to consider only Fourier coefficients of potential for the 50 shortest reciprocal lattice vectors in the iterative procedure to achieve self-consistency. The convergence of the exchange potential was found to be somewhat more rapid than that for the Coulomb potential.
2.2.3 Momentum Distribution of Electrons

Recently there has been a renewed interest in the Compton scattering experiments in solids. Unlike X-ray scattering factors, which are insensitive to the outer electron charge density, the Compton measurements are sensitive to the momentum distribution of outer electrons. Thus the Compton scattering experiments can provide a critical test for the wavefunctions from energy band calculation.

Platzman and Tzoar [87], by considering time dependent scattering theory justified the use of the impulse approximation in the theory of Compton line shape. The result can be summarised as follows: The impulse approximation is valid if:

1. The wavelength of the incident photon is so short that it interacts with only a single electron and ejects it instantaneously from the Fermi sea,
2. The energy transferred to the electron is large enough that the collision time is much shorter than the time required for any rearrangement of the remaining electrons.

The net effect is that the photon exchanges energy and momentum with a single electron in a constant potential field. The differential scattering cross section of photons from a system of electrons in solid can be shown to be

$$\frac{d\sigma}{d\omega d\Omega} = \frac{e^2}{mc^2} \left( \frac{\omega_2 - \omega_1}{\omega_1} \right) \frac{m}{|K|} \frac{1}{\Omega} J_4(q)$$ ...(2.33)

The Compton profile is given by

$$J_4(q) = \frac{\Omega}{(2\pi)^3} \int d^3P \rho(P) \frac{\delta(q-p*K)}{\delta(p)}$$ ...(2.33a)

with $K = \frac{\mathbf{K}}{|\mathbf{K}|}$

$$\text{with } K = \frac{\mathbf{K}}{|\mathbf{K}|}$$ ...(2.33b)
where the second summation runs over all reciprocal lattice vectors $K_s$, $a_n(g)$ is the expansion coefficients of the crystal wavefunctions, and $X_i(P)$ is the Fourier transform of the atomic wavefunctions $u_i(x)$

$$X_i(P) = \frac{1}{\sqrt{\Omega}} \int e^{iP\cdot r} u_i(x) \, dr \quad \text{(2.36)}$$

The expressions for $X_i(P)$ are given in appendix A. The integral in Eq.(3.33a) implies that the Compton profile measures the number of electrons having a fixed value of momentum in the direction of the photon's scattering vector $\hat{k}$.

Neglecting the spin-orbit interaction, the expansion coefficients $a_n(g)$ have been tabulated for 89 independent points in 1/48th of the Brillouin zone. The summation over all $g$ in the Brillouin zone may be expressed in terms of a sum over $g$ in the primitive 1/48th of the zone and a sum over group operations which generate the star of $g$. The symmetry properties of the Bloch function can then be used to transform the variables of integration. The final form of the expression for the Compton profile is

$$J_k(q) = \frac{\Omega}{(2\pi)^3} \sum_{n \text{ occu }} \int d^3g \sum_{K_s} |\Sigma a_n(g)X_i(g+K_s)|^2 \delta[q-g+K_s] \Sigma \delta[\beta K] \quad \text{(2.37)}$$

The sum over $\beta$ includes all operators in the cubic point group. If a GTO involves factor $\exp(-\alpha r^2)$ its Fourier transform will be proportional to $e^{\alpha q^2 \hat{a}^\dagger}$. These factors govern the convergence of the sum over reciprocal lattice vectors in Eq.(2.34a). For band states, the effective $\alpha$'s are not large and good convergence is obtained. However, convergence is much slower for core functions where large
Chapter 2

\( \alpha \)'s are encountered. A check on convergence can be obtained from the normalization condition on \( J_K(q) \):

\[ \int J_K(q)dq = n_e \text{ ...(2.38)} \]

where \( n_e \) is the number of electrons per atom. In our calculation, the sums over \( K \) were carried out over approximately 3000 permuted reciprocal lattice vectors. No contribution was included from the 1s wavefunctions (the impulse approximation is probably not valid for 1s electrons in X-ray Compton scattering measurements). The convergence of the reciprocal lattice sum for the band (4d and 5s) electrons is quite good; however, it is not complete for the core electrons. There remain small contributions mostly from the core electrons, that have been neglected. Consequently, the theoretical curves are probably slightly too low. This effect will be important mainly for larger values of \( q \) than are studied here. The contribution from the 1s electrons was determined using atomic wavefunctions.

The Compton profile in [100], [110], and [111] directions are shown in figures 3.5, 3.6, 3.7 for strontium, figures 3.19, 3.20, 3.21 for technetium and figures 3.33, 3.34, 3.35 for ruthenium. The total Compton profiles is shown in figures 3.4, 3.18, 3.32. The difference in Compton profiles along different directions is also illustrated in figures 3.9, 3.10, 3.11 for strontium, figures 3.23, 3.24, 3.25 for technetium, figures 3.37, 3.38, 3.39 for ruthenium. Considerable structure is evident in the curves. Much of this structure can be attributed to Fermi surface effects [88]. The momentum density \( \rho(P) \) suffers some discontinuity whenever \( P \) touches a piece of Fermi surface. For a fixed direction of momentum \( K \), the Compton profile \( J_K(q) \) measures the amount of the momentum density, contained in a plane perpendicular to \( K \), sweeping through the momentum space. The profile will have a cusplike behavior when the plane perpendicular to \( K \) happens to be tangent to a piece of flat Fermi surface. A thorough measurement on the Compton line shape can therefore provide information on the shape of the Fermi surface. Similar structures corresponding to Fermi surfaces in the higher order of the Brillouin zone should exist for larger values of \( q \). The sharpness of the breaks

in $J_x(q)$ indicates the amount of discontinuity presented in $\rho(P)$. The periodicities in the anisotropy of the Compton profile along different directions reflect the position of the reciprocal lattice vectors and hence the size and structure of the primitive cell. Of course many body effects would be expected to reduce the visibility of these structures through the introduction of additional high momentum components into the band wavefunctions.

The Compton profile along the [1,0,0] direction is relatively smooth since most of the Fermi surfaces parallel to this direction being moderately spherical. (see Figures 3.5, 3.19, 3.33). The structures presented in $J[1,1,0](q) - J[1,0,0](q)$ can be understood based on the Fermi surface effects along the [1,1,0] direction. The fine structure near the origin reflects anisotropy in the dimensions of the X hole pockets.

Finally the structures in $J[1,1,0](q) - J[1,1,1](q)$ can be interpreted as the combination of the Fermi surface effects. The spherical averaged Compton profile was obtained using sixth order Kubic harmonic expansion. The spherical average $J_{av}(q)$ was approximated as the zeroth order term in the expansion.

The contribution from the atomic core states that we used to add from the experimental measurements.
2.3 COMPUTATIONAL DETAILS

2.3.1 Choice of the basis function

The choice of the basis set is critical to a calculation using LCGO method. As suggested by Wang and Callaway [78] the exponents and coefficients given by Wachters [89] were used by Callaway and co-workers [90-93] and were found to give good results. In the present calculations, 16 s, 12 p and 8d exponents are used with an additional 1 f exponent for all for the reason mentioned in sec. 1.3. Small exponents required to describe the tails of atomic wave functions are not desirable in the present case of transition metals. The basis is tested for approximate linear dependencies prior to use by diagonalizing the overlap matrix $S_0(k)$ and checking if undesirably small eigenvalues develop.

After testing a number of basis sets, a selected set of exponents are used. In order to avoid any drastic modifications in the BNDPKG programme, one p and one d exponents are added. The values of the exponents used in the present work are given in Table 3.1, 3.6 and 3.12 respectively.

2.3.2 Fourier coefficients of the crystal potential.

The program for computation of Fourier coefficients is identified by FCOF name. The band calculation assumes as a starting approximation that the charge density is that of an assembly of neutral atoms arranged on lattice sites. The electron distribution pertaining to any single atom is assumed to be spherically symmetric. Possible departures from spherical symmetry due to open atomic shells are ignored. Fractional occupancy of shells is permitted. Let $\rho_s(r)$ represents the assumed atomic charge density. The Fourier coefficients of the Coulomb potential, including the nuclear term, are given by

$$V_c(K) = \frac{-8\pi Z}{\Omega K^2_s} + \frac{32\pi^2}{\Omega K^3_s} \int_0^\infty \rho_s(r) \sin(K_r) r dr$$

...(2.39)
for $K_s = 0$ is treated as a continuous variable, and allowed to approach zero, a finite limit is obtained. This value is taken as the definition of

$$V_c(0) = \frac{16\pi^2}{\Omega} \int \rho_s(r) r^4 dr$$

...(2.40)

$$\delta_\sigma(r) = (4\pi)^{-1} \sum n_{\sigma} |R_\sigma(r)|^2$$

...(2.41)

where the $n_{\sigma}$ are occupation numbers for atomic states of spin $\sigma$ and the radial wavefunctions $R_\sigma$ are expressed as linear combinations of gaussian orbitals:

$$R_\sigma(r) = \sum a_{ij} \sum N_j r^i \exp(\alpha_j r^2)$$

...(2.42)

in which the $a_{ij}$'s are the expansion coefficients for the atomic wave function, and the $N_j$'s are given by Equation (2.9). The number of orbitals included is $J$. Equations (2.41) and (2.42) are substituted in (2.39). Then,

$$V_c(K_s) = \frac{-8\pi Z}{\Omega K_s^3} + \frac{8\pi}{\Omega K_s^3} \sum a_{ij} \sum N_j N_j I_{11}(\alpha_j^+ \alpha_j, K_s)$$

...(2.43)

$$I_{11}(\alpha, K_s) = \int r^{|n|-1} \exp(-\alpha r^2) \sin(K r) dr$$

...(2.44)

The Fourier coefficients of the Ewald potential $V_e(r)$ Equation (2.17) are given by

$$V_e(K) = \frac{-2\pi}{\Omega \beta_1^2} \left[ \frac{2\pi \alpha}{\Omega \beta_1} F_1[1, -\frac{1}{2}, -\frac{1}{2}] + \frac{3 K_s^2}{\Omega \beta_2^2} F_1[1, -\frac{1}{2}, -\frac{3}{2}, \frac{3}{2}] \right]$$

...(2.45)

in which $F_1$ is the confluent hypergeometric function. The computation of the Fourier coefficients of the exchange-correlation potential $V_{xc}$ is considerably more complicated than for the Coulomb potential because of the presence of $\rho^{10}$. The general expression, which is obtained from (2.3) is

also $V_e(0)$ is defined as

$$V_e(0) = \frac{2\pi}{3\Omega} \sum \eta_{i\sigma} \sum a_{ij} a_{ij} N_j N_f \frac{\Gamma(1i+5/2)}{(\alpha_i^+\alpha_j^+)^{i(i+5/2)}}$$  ...(2.46)

$$V_{xc}(K_x) = (\Omega)^{-1} \int V_{xc}(r) \exp(-iK_x r) \, d^3r$$  ...(2.47)

The charge density involved here has to be constructed by adding (numerically), at selected points along specified directions in a unit cell, the contributions from atomic charge densities are placed on lattice sites $R_n$ such that $(2R_n / a)^2 < \text{MAXR}^2$. The exchange-correlation potential is expanded in cubic harmonics belonging to the $T_1$ representation [80] including up to 8 order harmonics.

$$V_{xc}(\mathbf{r}) = \sum_{i=0}^8 f_i(r) K_{i1}(\mathbf{r})$$  ...(2.48)

Since four values $(0, 4, 6, 8)$ are in this sum, the exchange correlation potential has to be computed in four independent directions. The functions $f_i(r)$ decrease rapidly as $r$ becomes small.

Figure 2.2 Schematic diagram showing the division of the irreducible wedge into three regions, with a cubic mesh constructed in the outer region (from Wang and Callaway [78]).
Figure 2. 2 Schematic diagram showing the division of the irreducible wedge into three regions, with cubic mesh constructed in the outer region (from Wang and Callaway [78].

The exchange-correlation potential is spherically symmetric to a high degree of accuracy near a nucleus. In the region I, near the nucleus only $f_0$ need be retained. The radius $r_1 = 1$ a.u. is found to be satisfactory for transition metals [78]. The contribution to the Fourier co-efficients of the exchange-correlation potential from regions I and II can be expressed in terms of radial integrals. The result is denoted as $V_{xc,I+II}(K_r)$

\[
V_{xc,I+II}(K_r) = \sum G_i(K_r)K_{i,i}(K_r)
\]  \hspace{1cm} (2.49)

\[
G_i(K_r) = i^i \frac{4\pi}{\Omega} \int f_i(r) j_i(K_r r) \text{ d}r
\]  \hspace{1cm} (2.50)

and $j_i$ is a spherical Bessel function. The integrals in (2.47) are done numerically, using Filon's rule. Finally the interstitial region III between the sphere and the cell boundary is considered. The $V_{xc}$ region is divided into small cubes of side $2d$. Within each cube is treated as a linear function of position. Also since the potential as $r$, symmetry, the contribution from a single cube can be written as

\[
V_{xc,\text{cube}}(K) = (\Omega)^{-1} \int V_{xc}(r_0) \nabla V_{xc}(r_0) \cos(K_x x) \cos(K_y y) \cos(K_z z) \text{ d}^3r
\]  \hspace{1cm} (2.51)

Where $r_0$ is the centre of cube. A linear approximation $V(r)$ has been used in the last step. The integrals over the cubes are elementary and can be done analytically. Thus the size of the cubes required for a given accuracy is determined by the potential and the rapid variation of the trigonometric function is irrelevant. Each cube is assigned a weight factor, which is the fraction of the cube volume, which lies within the irreducible wedge (1/48th) of the unit cell and is also outside of the inscribed sphere bounding region II. The portion outside the sphere is calculated in an approximation in which the portion of the spherical surface within the cube is replaced by a plane.

The accuracy of these fairly involved procedures has been tested by applying these to the charge density [78]. The largest error observed amounts to about 0.01% where.
2d/a = 1/48 in comparison with that of the method incorporated in Equation (2.45). For very large values of $K_s$, the rapid oscillations of the spherical Bessel functions lead to small values of the Fourier coefficients. Furthermore, there are frequently different types of RLVs with wave vectors of the same magnitude. MAXK2=4000 is used in case of FCC. For $(aK_s/2\pi)^2 >$MAXK2 only $f_s$ is retained in (2.48), and the integral is performed in the Wigner-Seitz sphere (the sphere whose volume equals the volume of the unit cell). The large $K_s$ Fourier coefficients are required only in the evaluation of central cell overlap integrals for s-s, p-p, and d-d cases. The Fourier coefficients of $\rho_0^{-25}$ which are required for the computation of charge in the Fourier coefficients of the exchange-correlation potential, Equation (2.24), are calculated in the same way as those of $\rho_0^{10}$. This procedure is incorporated in the program FCOF in BNDPKG.

2.3.3. Hamiltonian and overlap integrals.

The program for computation of these integrals is recognized by name (ESINT)

The second programme ESINT in BNDPKG is to compute hamiltonian (Kinetic energy, Coulomb potential, and exchange correlation potential) and overlap integrals (Equation 2.12, 2.13 and 2.15). Explicit expressions for the general integral have been described by Wang and Callaway [78] and will not be elaborated here. Incorporating the cubic symmetry, the integral is written as

$$I_{ij}(K,A,B,C) = \int u_i (r-A) \cos (K_x x_i) \cos (K_y y_i) \cos (K_z z_i) u_j (r-B) d^3r \quad \text{(2.52)}$$

in which the $u_i$ have the form

$$u_i (r-A) = x^m y^n z^n \exp \left( -\alpha_i r_i^2 \right) \quad \text{(2.53)}$$

$$u_j (r-B) = x^q y^s z^t \exp \left( -\alpha_j r_j^2 \right) \quad \text{(2.53)}$$

where $A, B$ and $C$ are lattice sites. The indices $i, j$ are used to represent the triples...
of numbers \((l,m,n)\) and \((q,s,t)\), respectively, and \(r_A = r - \Delta = (X, Y, Z)\) etc. The cubic symmetry of Hamiltonian allows one to use Equation (2.52), which can be evaluated in cartesian co-ordinates. It is the product of three similar integrals of which it is enough to consider only one:

\[
\int x_A^q x_B^q \exp[-\alpha_1 x_A^2 - \alpha_2 x_B^2] \cos(Kx)dx
\]  

...(2.54)

This integral is rewritten using the identity in which the following definitions are used.

\[
\exp[-\alpha_1 x_A^2 - \alpha_2 x_B^2] = \exp\left[\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} (AB)^2\right] \exp[-(\alpha_1 + \alpha_2)x^2] 
\]  

...(2.55)
\[
\exp[-\alpha x^2 - \alpha_2 x^2_b] = \exp \left[ \frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} (AB)^2 \right] \exp[-(\alpha_1 + \alpha_2) x^2_b]
\]

...(2.55)

\[\Delta B = B - A, \quad D = \frac{\alpha_1 \Delta + \alpha_2 B}{\alpha_1 + \alpha_2}
\]

...(2.56)

It is possible to shift the origin for the integration to \(D\) using

\[r_A = r_D + \Delta D
\]

and a binomial expansion. Then, (2.54) is expressed as

\[
\varepsilon_\chi = \sum_{ab} \binom{l}{a} \binom{q}{b} (AD)_x^{1-a} (BD)_x^{q-b} \int_{-\infty}^{+\infty} \exp[-(\alpha_1 + \alpha_2) x^2] dx
\]

...(2.57)

\[x^{ab}[\cos(K_\chi)(CD)_x \cos(K_\chi) - \sin(K_\chi)(CD)_x \sin(K_\chi)] dx
\]

\(\binom{l}{a}\) is a binomial coefficient and

\[
\varepsilon_\chi = \exp[-(\alpha_1 \alpha_2)/(\alpha_1 + \alpha_2)]
\]

...(2.58)

The integrals can now be expressed in terms of Hermite polynomials. Equation (2.57) becomes

\[
\varepsilon_\chi = \sum_{ab} \binom{l}{a} \binom{q}{b} (AD)_x^{1-a} (BD)_x^{q-b} G_{st} \left[ K_\chi(CD)_x \right]
\]

...(2.59)
Chapter 2

\[ G_{a+b} \left[ K_{x},(CD)x \right] = \frac{(-1)^{(a+b)/2}}{2^{(a+b)}} \left[ \frac{\pi}{\alpha_1 + \alpha_2} \right]^{1/2} \frac{1}{(\alpha_1 + \alpha_2)^{(a+b)/2}} \]

\[ \exp \left[ -\frac{K^2_x}{4} (\alpha_1 + \alpha_2) \right] H_{a+b} \left[ \frac{K_x}{2\sqrt{\alpha_1 + \alpha_2}} \right] \cos(K_x)(CD)_x \]...

If \( a+b \) is even, and

\[ G_{a+b} \left[ K_{x},(CD)x \right] = \frac{(-1)^{(a+b)/2}}{2^{(a+b)}} \left[ \frac{\pi}{\alpha_1 + \alpha_2} \right]^{1/2} \frac{1}{(\alpha_1 + \alpha_2)^{(a+b)/2}} \]

\[ \exp \left[ -\frac{K^2_x}{4} (\alpha_1 + \alpha_2) \right] H_{a+b} \left[ \frac{K_x}{2\sqrt{\alpha_1 + \alpha_2}} \right] \sin(K_x)(CD)_x \]...

If \( a+b \) is odd

The final result of \( I_{ij} \) is

\[ I_{ij}(K,A,B,C) = \exp \left[ -\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} (AB)_i^2 \right] \sum_{abcdef} \left( \frac{1}{a} \right)^{(q-b)}(c) \]

\[ G_{a+b} \left[ K_{x},(CD)_x \right] G_{c+d} \left[ K_{y},(CD)_y \right] G_{e+f} \left[ K_{z},(CD)_z \right] \]...

The elements of the overlap matrix are found by setting $k=0$ in Equation (2.62). The kinetic energy matrix elements are found by differentiating the overlap matrix elements with respect to the lattice coordinate. The integrals involving the exchange-correlation potential can be found from Equations (2.15), (2.32) and (2.62) with due allowance for the construction of symmetrized combinations of plane waves. This merely leads to a numerical factor in forming the sum, as all coefficients $V(\beta K_s)$ are equal for all rotations $\beta$ in the point group of the crystal.

A study of Equations (2.60) and (2.61) reveals that the convergence of the series (2.15) for a given $V_{ij}(R_{ij})$, is controlled by the factor $\exp[-K^2/4(\alpha_1 + \alpha_2)]$. Another factor $\exp[-\alpha_1 \alpha_2 (AB)_x^2/(\alpha_1 + \alpha_2)]$ controls the order of magnitude of $V_{ij}(R_{ij})$.

A typical set of basis functions may contain a range of more than six digits in the quantities $\alpha$, running from (say) $\alpha=0.1$ to $\alpha=3 \times 10^5$. $K^2 < 4000$ for FCC are used (The factor $2\pi/a$ in the definition of $K$ is usually close enough to 1 to be disregarded for the purposes of a classification of condition). There are three cases.

1. $\alpha_1 + \alpha_2 < 25$ (roughly). Then the sum (2.15) converges rapidly enough so that the Ewald term is not required. The sum is carried up to

$$K_s^2 = 4[(\alpha_1 + \alpha_2)\text{EXPCVG} - \alpha_1 \alpha_2 (AB)_x^2]\text{EXPCVG} = 40$$

2. Both $\alpha_1$ and $\alpha_2$ large ($>25$). In this case the sum (2.15) is slowly convergent, but only the “Central cell” ($\Delta = \beta$) integral is important. The Ewald technique is necessary but quite simple to apply.

3. $\alpha_1$ large and $\alpha_2$ small (or interchanged). This estimation is the most complex. It corresponds to the overlap of a localized wavefunction by an extended function. The Ewald term is included.

In cases (2) and (3), the series (2.15) is summed up to $K_s^2 = (2\pi/a)^2 K2\text{MAXM}$ for the difference between the actual Coulomb potential and the Ewald potential and also for the exchange-correlation potential. Larger values of $K_s$ are included by

numerical integration using Simpson's rule (central cell only). A real space integral has to be done with the additional potential $V_x(r)$ (Equation (2.17)) and is discussed by Wang and Callway [78].

2.3.4 Matrix elements

The calculation of matrix elements involves a sum over lattice sites of the orbital integrals computed in the previous section, with the appropriate Bloch phase factor. Thus,

$$H_j(k) = \sum \exp(-ik \cdot R_p) E_j(R_p)$$  \hspace{1cm} (2.63)

and similarly for the overlap. At first sight this sum is exceedingly complicated because, (1) the phase factor is complex, and (2) all lattice sites are involved. However, use of the rotational symmetry properties of Hamiltonian and of the orbitals leads to enormous simplifications.

Let $\beta$ be one of the operations of the point group of the crystal; in this case, the 48 member cubic groups $O_h$. The Hamiltonian is invariant under any such rotation, and is written as

$$H(\beta \tau) = H(\tau)$$  \hspace{1cm} (2.64)

The orbitals $u(\tau)$ obey $u(\beta \tau) = \sum D_{\beta \tau} \ u(\tau)$  \hspace{1cm} (2.65)

where $D_{\beta \tau}$ are the representation matrices which are relevant to the orbitals. It follows that

$$E_j(\beta \cdot R_p) = \sum D_{\beta \tau} \ D_{\tau \beta}^{-1} \ D_{\beta \tau} \ E_j(R_p)$$  \hspace{1cm} (2.66)

An additional rule follows from the hermiticity of the Hamiltonian.
\[ E_j(R) = E^*_{ji}(-R) \] 

Equations (2.66) and (2.67) can be used to reduce the number of independent integrals \( E_j \) which have to be evaluated, and also to simplify the summation over lattice vectors in (2.11a). The steps to be followed are to decompose the sum over direct lattice vectors into:

1. a sum over rotationally independent vectors (different type) and
2. a sum over those vectors which can be obtained by point group rotations.

Equations (2.66) and (2.67) are to be used to simplify the latter sum as much as possible.

Elements of the Hamiltonian matrix are arranged according to the angular symmetries in the following way: \( d, s, p, f \). It is possible that some of the elements are imaginary. This occurs if the element connects orbitals of opposite parity. The Hamiltonian matrix, in Bloch form, is written as:

\[
H = \begin{bmatrix}
H_{dd} & H_{sd} & iH_{pd} & iH_{fd} \\
H_{sd} & H_{ss} & iH_{ps} & iH_{fs} \\
-iH_{pd} & -iH_{ps} & H_{pp} & H_{fp} \\
-iH_{fd} & -iH_{fs} & H_{fp} & H_{ff}
\end{bmatrix}
\]

in which the submatrices are real and symmetric, and the \( i \)'s are shown explicitly.

A unitary transformation \( U \) is introduced, and a transformed Hamiltonian is generated according to:

\[ H' = UHU^* \]

\[ \text{U is chosen to be of the form} \]

The transformation amounts to a change in phase factor of \( p \) and \( f \) orbitals in the basis. The transformed Hamiltonian is

\[
U = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & i & 0 \\
0 & 0 & 0 & i \\
\end{bmatrix}
\]  

...(2.70)

The problem to be solved by diagonalization is

\[
HX = SXA
\]  

...(2.72)

In the programme (BND) the lower triangle of the real symmetric matrix (2.71) is calculated. The \( k \) dependent matrix elements of the Coulomb potential of the charge distributions including both nuclei and electrons, exchange-correlation potentials, kinetic energy and overlap are calculated and stored for use in self consistency part.

In which \( H \) and \( S \) are the Hamiltonian and overlap matrices in real form (2.71). \( X \) is the eigenvector matrix and \( \Lambda \) is the diagonal matrix of eigenvalues. \( S \), being positive
definite, is first decomposed into upper and lower triangular matrices U and L,

\[ S = LU \]  \hspace{1cm} (2.73)

From the above equations, one can write

\[ H''X'' = X''A \]  \hspace{1cm} (2.74)

where \( H'' = L^{-1}HU^{-1} \) and \( X'' = UX \). The transformed hamiltonian \( H'' \) is diagonalized using the scientific subroutine available in the computer system.

2.3.5 Generalized overlap integrals. (SIJ)

The program to compute this is named SIJ. These are the integrals required in order to determine the changes in charge density as the iterations progress toward self consistency. The Equation (2.22) can be expressed as

\[ S_{ij}(k,k_0) \sum \exp (ik \cdot R_p) \int u_i^*(r-R_p) \phi(k_0,r)u_j(r) d^3r \]  \hspace{1cm} (2.75)

where

\[ \phi(k_0,r) = \eta_s \sum_p \cos (K_{sx}x) \cos (K_{sy}y) \cos (K_{sz}z) \]  \hspace{1cm} (2.76)

in which \( \sum_p \) indicates that the sum is over distinct permutations of the positive numbers \( K_{sx}, K_{sy}, K_{sz} \). \( \eta_s \) stands for the number of terms, after incorporating the symmetry, in Equation (2.76). It follows that the generalized overlap integrals are expressible in terms of the general integral \( I_{ij}(K,A,B,C) \) defined by Equation (2.52). Let \( A=R_p \) in Equation (2.52). Then one gets

\[ \int u_i^*(r-R_p) \phi(k,r)u_j(r) d^3r = \eta_s \sum I_{ij}(k,R_p,0,0) \]  \hspace{1cm} (2.77)

in which $\Sigma$ has the same meaning as in (2.76). It is still necessary to carry out the sum over $\mathbf{R}_u$ in (2.77). The function $\phi$ and $\Gamma_i$ has symmetry which is the same symmetry as that of the hamiltonian. Therefore, the sum over $\mathbf{R}_u$ is carried out as in (Section 2.3.4). The factors of $i$ which arise in the process, however, are cancelled by the unitary transformation (2.69). For reasons of computational convenience, the programme SIJ generates all the $S_{ij}$ as the $\mathbf{k}$ varies over the Brillouin zone (BZ) for fixed $\mathbf{K}$, then $\mathbf{K}$ is incremented, and the process is repeated. But, the results are written in order of increasing $\mathbf{K}$, for fixed $\mathbf{k}$. Only lower triangle of $S_{ij}$ is stored because of symmetry. This programme has been used in testing the basis set for the linear independence. This is done by diagonalizing the overlap metrix, i.e. $S_{ij}(k,0)$ for a selection of points $k$ in the BZ. If the eigenvalues are less than $10^{-4}$ the basis is revised.

2.3.6 Self consistency

The iterative self-consistency programmes (SCF1 or SCF2) given in BNDPKG combine elements computed in the previous programmes and produce self-consistent band structures. SCF1 is used for systems without spin polarization and SCF2 for ferromagnetic systems. In this part the linear analytic tetrahedron method [94-97] is employed for numerical integration over the BZ. This method is discussed in detail by Wang and Callway [78].

The essential output of each iteration is a set of Fourier coefficients of the changes in the Coulomb and exchange-correlation potentials, calculated in that iteration with respect to the starting potentials assumed by FCOF. It has been observed that $\delta V(\mathbf{K})$ is reasonably rapidly convergent, so that 20-100 rotationally independent $\mathbf{K}$ usually suffice. This reflects the physical fact that readjustments of the outer electrons vary much.

Unfortunately, it frequently happens that if the changes $\delta V(\mathbf{K})$ are simply cumulated from the stage to stage, process will diverge. In order to obtain convergence, the computed change in potentials is multiplied by a factor $\text{FACT}(\leq 1)$. Thus, the change in potential passed on to the next stage of iteration (say $1+2$) is computed from those of the present ($1+\ldots$) and preceding ($1$) stages according to

FACT * \( \delta V(1+1) + (1-\text{FACT}) * \delta V(1) \).

Before beginning the calculations of the \((1+1)\) stage, it is possible to modify the potential transferred from the 1th stage by changing the value of the multiplier FACT used in that stage. In outline, both SCF programmes proceed as follows:

1. The tetrahedral mesh used in integrations over the BZ is defined.
2. The Fourier coefficient of the starting (non self-consistent) potential are read.
3. The corrections to the original potential from previous iterations are read and the results from the last stage are adjusted by the corresponding ratio.
4. For each \(k\) considered the original Coulomb potential, kinetic energy, exchange-correlation and overlap matrices are read (output of BND) and the non self-consistent hamiltonian is constructed.
5. The elements of the hamiltonian are revised to include the corrections to the potential generated in the last iterative cycle. This process involves the generalised overlap matrices \(s_{ij}\) previously generated, thus

\[
H_{ij}(k) = H_{ij}^{(0)}(k) + \sum_{g} \left[ \delta V_e(K_g) + \delta V_{xc}(K_g) \right] s_{ij}(k,K_g)
\]

\[(2.78)\]

in which \(H^{(0)}\) is the non-self-consistent hamiltonian, \(\delta V_e\) and \(\delta V_{xc}\) are the corrections to the coulomb and exchange-correlation potentials, respectively, and the sum includes only rotationally independent reciprocal lattice vectors.

6. The hamiltonian is diagonalized and the fermi energy is calculated.
7. The corrections to the charge density, and hence to the Coulomb and exchange-correlation potentials, and exchange-correlation potentials, in the present iteration are obtained.

Table 2.1 Some of the input parameters used in the self-consistent band structure calculations for BCC and FCC structures.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>bcc</th>
<th>fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum $R^2$</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Maximum $K_x$</td>
<td>3000</td>
<td>4000</td>
</tr>
<tr>
<td>Number of $k$ points in $(1/48)^{th}$ of the BZ</td>
<td>55</td>
<td>89</td>
</tr>
<tr>
<td>Number of $k$ points for final band structure</td>
<td>506</td>
<td>505</td>
</tr>
<tr>
<td>Number of independent RLV's for self-consistent correction</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Number of iterations for self-consistency</td>
<td>36</td>
<td>36</td>
</tr>
</tbody>
</table>

The above processes are repeated to get convergence. In the present work the iterations are continued until the change in potentials $\delta V_c$ and $\delta V_{xc}$ varied only in the sixth decimal place. The value of the FACT is varied from 0.1 to 0.3, at different stages. The calculations are carried through 36 iterations for all the metals. Some of the parameters used in the present calculation are enumerated in Table 2.1.

We have presented band structure of Ru in the bcc phase also and presented it in appendix B.

2.3.7 Final band struture.

After the conclusion of the iterations leading to self-consistency. The final band structure is obtained at a large number of points (505 for FCC and 506 for BCC) in the zone. In order to do this the changes in the potential are incorporated in the construction of a revised set of hamiltonian integrals using the programme ESINT with revised input parameters. The programme BND is then executed using the revised integrals, and the resulting energy levels and wavefunctions are stored for further use. The density of states is calculated using the analytical tetrahedron method.