NON-SPHERICAL POTENTIALS IN THE BAND THEORY OF SOLIDS

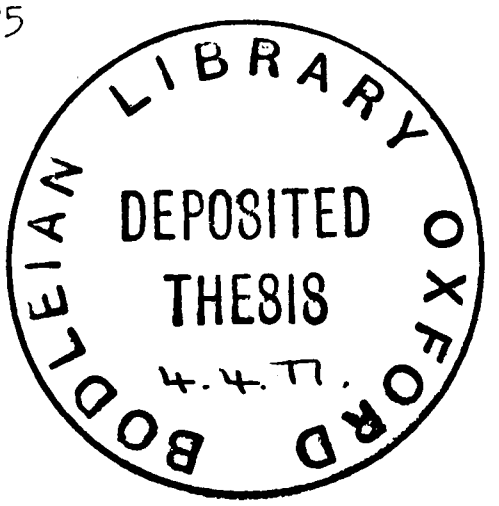
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ABSTRACT

This study is concerned with the problem of calculating electronic band structures of solids from a priori potentials, in particular potentials which are not spherically symmetric about the centre of the Wigner-Seitz cell. Band structure calculations are performed using the Cellular Method, and the adaptation of this method to deal with non-spherical potentials is a major concern of this work.

A review is presented of the work so far published on non-spherical potentials in the OPW, APW and KKR methods, and the ideas to be built on in the present work are considered more carefully. The details of the Cellular Method are expounded, paying particular attention to the stages which require modification in the non-spherical treatment.

The superposition method introduced by Mattheiss, and by which many of the potentials used in band structure calculations are constructed from the appropriate atomic potentials, is extended to include non-spherical terms, and a general expression for the potential is obtained for the f.c.c. lattice. This expression takes the form of an expansion in spherical harmonics correctly orientated with respect to the crystal axes.

We then proceed to consider the non-spherical corrections introduced when the potential used in the Cellular Method is the true potential within the whole circumscribing sphere of the Wigner-Seitz cell, which overlaps the neighbouring cells. These non-spherical corrections to the potential are non-zero in the region between the inscribed and circumscribing spheres of the cell, and therefore affect the radial wave functions over this region - the very region over which their values are required in order to perform the boundary condition fitting of the Cellular Method.

Methods are developed for the treatment of general non-spherical potentials which can be written in terms of a reasonably convergent expansion in spherical harmonics. First of all a rigorous

treatment, in which it is found necessary to label the radial functions with two sets of angular momentum quantum numbers is developed. This treatment involves the calculation of many more radial functions than the usual spherical treatment and the form of trial function produced necessitates certain changes and generalisations of the Cellular Method. It is, therefore, important to look for possible approximations which might be employed to facilitate a quicker, and more simple solution to the problem. Two such methods are explored.

A suite of computer programs is set up to deal with the calculations necessary to employ the methods developed, and these programs are described in some detail. The methods are then applied to the non-spherical correction arising from the strict division of the potential field into cells mentioned above, using the potential of Chodorow for f.c.c. copper as a basis. Various tests of the methods developed are undertaken. An iterative approach to the problem, much quicker to compute than the rigorous treatment, is shown to give results in excellent agreement with those of the rigorous treatment for the case considered, and is certainly worthy of further investigation in cases where the non-spherical corrections are larger. Both of these treatments are shown to retain adequate convergence of the cellular expansion.

The corrections due to the newly proposed potential scheme are shown to be often negligible, and never more than 0.008 Rydbergs, for the lower lying band energies at the symmetry points in $\underline{k}$-space calculated.

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CHAPTER 1

INTRODUCTION

1.1. The Background to this Study

Over the last forty years, band structure calculations of varying complexity have been undertaken by a variety of different methods. The textbook of Ziman (1964) provides a good introduction to many of these methods, whilst a longer review is given by Pincherle (1961). The most popular of the methods have been the "Augmented Plane Wave" (APW) method, the "Green Function" (KKR) method, the "Orthogonalised Plane Wave" (OPW) method and the "Cellular" method. Each of these methods has been seen to be a valid and accurate approach to the band structure problem, and more important now are the assumptions made about the potential field in which the electrons of the solids move.

Most of the procedures have traditionally used the well known "muffin tin potential approximation", that is non-intersecting spheres around each atom with a spherical potential within, and a constant potential outside (in practice the zero of energy is usually taken to be this constant potential, so that the model then has zero potential outside the spheres). The spherical potential is usually built up by some superposition method which takes account of the potentials due to neighbouring atoms about any chosen central atom (such a method will be derived in detail in Chapter 3). There are two variable parameters in these muffin tin approximations, the first being the radius of the muffin tin sphere (or atomic sphere, as it is often called), which is limited by the fact that these must not intersect, and the second being the value of the constant potential between the spheres, which has not necessarily to be continuous with the potential within the spheres - though it would seem both unphysical, and mathematically unsound to allow such a discontinuity. We shall have more to say about these variable parameters in the work which follows.

For materials with a high coordination number, this model should be adequate, and has indeed been successful in many types of band structure calculation, as we shall see through the course of this work. However, for materials with low coordination number, such as the diamond structure where the muffin tin approximation would lead to the potential being constant over two thirds of the volume of the unit cell, this approximation is clearly an inadequate representation of the true situation. The covalent bonds in semiconducting materials will also imply large asymmetries in the electron density, and consequently the approximation of taking spherically symmetric potentials within the muffin tin spheres cannot be justified. Muffin tin spheres centred on nearest neighbours touch along the direction of the covalent bond, so the larger asymmetries are expected to be within these spheres. Indeed in some cases it would seem more appropriate to consider the spherical potential centred about the mid-point between the atoms. Keller (1971) has taken up this idea and considers the introduction of extra muffin tin spheres: atomic potential spheres in the regular lattice sites and hollow spheres, of potential higher than the muffin tin zero, in an interstitial sub-lattice. Until fairly recently band structure calculations for such materials have been almost exclusively undertaken by the OPW method, the basis of which will be described in the following section. The OPW method has generally been applied to a crystal potential which is the sum of spherical potentials on various atomic sites, much nearer than the muffin tin approximation to the true self consistent form. However, as we shall discover, the OPW method does have disadvantages, and it is therefore desirable to find suitable alternatives.

It has for some time been recognised that the muffin tin form is in no way essential to the popular APW or KKR methods. Indeed, Beleznay and Lawrence (1968) have shown that both methods can be easily adapted to deal with a potential which is not flat outside the atomic spheres. More recently, much work has been done in further adapting these

methods to include not only non-flat potentials in the interstitial regions, but also non-spherical potentials within the spheres; much of this work will be referred to in the following sections.

We now turn to the Cellular Method, as implemented by Altmann (1974), and consider its adaptation to non-muffin tin potentials. We discover, on preliminary consideration that the method should contain corrections to the potential in the constant region around the usual atomic spheres - that is the inscribed spheres of the unit cells. This correction has been neglected in the past, but will be developed during the course of this work, and shown to be small in the case of copper, where successful band structure calculations have already been completed using the Cellular Method, with the Chodorow muffin tin potential (see Burdick, 1963). The Cellular Method has also, in the past, been applied successfully to a potential spherical out to the circumscribing sphere of the unit cell (see work on calcium by Altmann et al. 1971 and 1972), where the non-spherical corrections can also be calculated in the same way by the methods to be developed.

It will become clear that one of the major problems in dealing with non-spherical potentials is the calculation of radial wave functions, which now become dependent on the azimuthal angular momentum quantum number, m. Once a method of solution is obtained, it will be valid for any of the major procedures of band structure calculation, and with this point in mind we shall devote the next three sections of this chapter to brief discussions of the OPW, APW and KKR methods and the non-muffin tin work which has recently been undertaken by these techniques. In these sections we do not attempt to present all the background, and the reader might find Chapter 2 a useful introduction to the formalism used here.

Section 1.5. will then describe the work which has been undertaken on the Cellular Method, to be expounded in detail in the following chapters. Finally, Section 1.6. will present a plan of the thesis.

1.1. The OPW Method

This method is comprehensively described in the review of Woodruff (1957), whilst more recent calculations using the method are presented by Herman et al. (1968), where the possibility of empirically adjusted potentials is also explored.

First consider crystal core wave functions built up from the atomic core states as Bloch functions,

$$\psi_{n\ell m;\underline{k}}(\underline{r}) = \frac{1}{\sqrt{sN}} \sum_{t} \exp(i\underline{k}.\underline{R}_t) u_{n\ell m}(\underline{r}-\underline{R}_t) , \qquad (1.2.1.)$$

where the lattice considered has N atoms, there are s atoms in volume V_o, and lattice sites are labelled by vectors $\underline{R}_t$. This is actually a solution of the Schrödinger equation of the whole crystal, corresponding to the core level of energy E_n. The higher states, as solutions of the same Schrödinger equation, must be orthogonal to the wave functions $\psi_{n\ell m;\underline{k}}(\underline{r})$, and also appear plane-wave-like between the atoms. Thus, consider the function

$$\chi_i = (NV_o)^{-\frac{1}{2}} \exp(i\underline{k}_i.\underline{r}) - \sum_{n\ell m} B_{n\ell m;\underline{k}_i} \psi_{n\ell m;\underline{k}_i}(\underline{r}) , \qquad (1.2.2.)$$

required to be orthogonal to the core function $\psi_{n\ell m;\underline{k}}(\underline{r})$, so that

$$B_{n\ell m;\underline{k}_i} = (NV_c)^{-\frac{1}{2}} \int \exp(i\underline{k}_i.\underline{r})\, \psi_{n\ell m;\underline{k}_i}(\underline{r})\, d\tau , \qquad (1.2.3.)$$

using the orthogonality of the core functions themselves. This should be a fair representation of the true situation, since the so formed orthogonalised plane wave will be plane-wave-like in the outer regions,

where the core functions are small, and yet orthogonal to the core functions within the atomic sphere. Note that, unlike the conventional APW method, the plane wave is allowed to extend into the spheres.

Finally a trial wave function is set up as a linear combination of such OPW's, giving

$$\Psi_{tr} = \sum_{j=0}^{s} a_j \chi_j \qquad (1.2.4.)$$

where the $\underline{k}_j$'s used differ by a reciprocal lattice vector from the $\underline{k}_i$ of the wave function required, and the lower limit to the energy is found by a variational method. Defining $W(\Psi_{tr})$ as

$$W(\Psi_{tr}) = \int \Psi_{tr} H \Psi_{tr} \, d\tau \geqslant E_0 \, , \qquad (1.2.5.)$$

and proceeding to minimise W, gives the requirement

$$\det[(\chi_i, H\chi_j) - W(\chi_i, \chi_j)] = 0 \, , \qquad (1.2.6.)$$

where we employ the notation

$$(f, g) = \int f^* g \, d\tau \, . \qquad (1.2.7.)$$

Here H is the appropriate Hamiltonian operator, containing the crystal potential $V(\underline{r})$. The value of s in the summation of equation (1.2.4.) is chosen sufficiently high to ensure the convergence of the variational result within the required limits. Woodruff next proceeds to show that the overlap integral, or Hamiltonian matrix elements, are given by

$$(\chi_i, H\chi_j) = k_i^2 \delta_{ij} + v(\underline{g}_j - \underline{g}_i) - \sum_{n,\ell} E_{n\ell} A^*_{n\ell}(k_i) A_{n\ell}(k_j) P_\ell(\cos\theta_{ij}) \sum_t \exp[i(k_j - k_i).\underline{R}_t] \, , \qquad (1.2.8.)$$

where

$$v(\underline{g}_j - \underline{g}_i) = (NV_0)^{-1} \int \exp[i(g_j - g_i).\underline{r}] V(\underline{r}) \, d\tau \, , \qquad (1.2.9.)$$

$$A_{n\ell}(k) = (V_c)^{-\frac{1}{2}} \int u_{n\ell;\underline{k}}(\underline{r}) \exp(i\underline{k}.\underline{r})\, d\tau \,, \qquad (1.2.10.)$$

and the $\underline{g}$'s are reciprocal lattice vectors. The approximation

$$H u_{n\ell;\underline{k}} = E_{n\ell}\, u_{n\ell;\underline{k}} \,, \qquad (1.2.11.)$$

where $E_{n\ell}$ is the free atom energy corresponding to $u_{n\ell;\underline{k}}(\underline{r})$, is made in writing this matrix element. A similar expression can be found for the (χ_i, χ_j) and the minimum value of W satisfying (1.2.6.) can be found. Note that the $A_{n\ell}(k)$, defined above and related to the $B_{\ell nm;\underline{k}}$, are not dependent on m for core wave functions which are spherical radial functions. The presence of an m-dependent radial function (as arises in the case of a non-spherical potential) would remove this simplification, but on the other hand presents no particular difficulty.

It is clear from equations (1.2.8.) and (1.2.9.) that the crystal potential only enters the calculation via its Fourier transform, and that there is in principle no simplification afforded by the potential being spherically symmetric. As mentioned above, the potential most commonly used is one of the form

$$V(\underline{r}) = \sum_t v(\underline{r} - \underline{R}_t) \,, \qquad (1.2.12.)$$

where $v(\underline{r})$ is the atomic potential around each individual atom, generally spherical, so that m-dependent radial core functions are not required.

It would seem from the above discussion that the OPW method should be used exclusively for band structure calculations, and that further research into other methods would be purely academic. However, this is not the case as the method does run into trouble in certain, none too few, applications. The convergence of the method is not so good in the case of

some ionic crystals, whose valence functions are poorly represented by plane waves. More seriously, the method has run into trouble when dealing with the 3d transition metals, since the 3d functions are, by symmetry, automatically orthogonal to all the core functions, so that the OPW reduces to a simple plane wave expansion. Callaway (1955 a and b) has shown how this difficulty might be overcome, modifying the OPW expansion by the addition of atomic d-functions which are made to vanish smoothly at the inscribed sphere of the unit cell. The problem then arises that the OPW's are no longer exact solutions of the Schrödinger equation within the sphere, and this probably contributes to the fact that the method still fails to converge as well as the APW method in such cases (Kleinman and Shurtleff, 1969).

1.3. The APW Method

The APW method was first formulated by Slater (1937), and though the principle of the method has remained the same many changes in form have taken place. For a comprehensive account, we refer the reader to the book by Loucks (1967). The method has been applied successfully in many cases, e.g. for copper by Burdick (1963).

The APW method was based on the muffin tin potential approximation, the muffin radius being such that the spheres do not intersect. The Schrödinger equation is solved exactly for the spherical potential within the spheres as an expansion in spherical harmonics, whilst plane waves provide the exact solutions in the volume between the spheres. These solutions are matched on the surface of each sphere, thus constructing a solution of the Schrödinger equation throughout the crystal.

For an energy E, the solution of the Schrödinger equation within each sphere is written in the form

$$\chi_{\underline{k}}^{in}(\underline{r}) = \sum_{\ell,m} i^{\ell} C_{\ell m}^{\underline{k}} R_{\ell}(r,E) Y_{\ell}^{m}(\hat{\underline{r}}) \quad , \quad r \leq r_o \ , \qquad (1.3.1.)$$

where the $Y_{\ell}^{m}(\hat{\underline{r}})$ are the well known spherical harmonics and the $R_{\ell}(r, E)$ are solutions of the radial equation which will be introduced in the following chapter, whilst the solution outside the spheres is

$$\chi_{\underline{k}}^{out}(\underline{r}) = \exp(i\,\underline{k}.\underline{r}) \quad , \quad r > r_o \ . \qquad (1.3.2.)$$

The $C_{\ell m}$ of equation (1.3.1.) must be chosen to match this solution to a single plane wave on the surface of the sphere, radius r_o. To do this the well known expansion of a plane wave in spherical harmonics is employed and we obtain

$$C_{\ell m}^{\underline{k}} = \frac{4\pi j_{\ell}(kr_o)\, Y_{\ell}^{m*}(\hat{\underline{k}})}{R_{\ell}(r_o,E)} \ , \qquad (1.3.3.)$$

where the $j_{\ell}(kr_o)$ are spherical Bessel functions, and k is the modulus of vector $\underline{k}$. Having formed the single APW, defined by equations (1.3.1.) to (1.3.3.), the trial solution is then formed exactly as in the OPW method, and a similar variational solution produced, using the variational expression derived by Schlosser and Marcus (1963) for the case where two basis sets are used - one inside and one outside the atomic spheres.

We have not considered the introduction of symmetry properties into this outline of the APW method. Clearly the Schrödinger equation solution of equation (1.3.1.) could be written as an expansion in terms of the symmetry adapted harmonics of the appropriate sub-group of the crystal lattice (see Section 3.7 below) as basis set. Also in the expansion in $\chi_{\underline{k}}(\underline{r})$ of the trial function, no two $\underline{k}$'s related by the symmetry of the crystal lattice must be included. The symmetrised APW method is

dealt with in detail by Mattheiss, Wood and Switendick (1968).

Much work has been done in extending the APW approach in the direction of non-muffin tin potentials. We shall refer to that of De Cicco (1967), Rudge (1969), Koelling (1969), Kleinman and Shurtleff (1969), Kane (1971), Evans and Keller (1971), and John, Lehmann and Zeische (1972). In all APW approaches, it has been necessary to distinguish between "non-flat" and "non-spherical" corrections to the muffin tin potential. This is so since the wave functions are produced, as shown above, in two basis sets, matched on the atomic spheres. Corrections in the plane wave region are referred to as "non-flat", and a potential containing only such corrections is referred to as a "warped muffin tin potential", as used by Koelling. Corrections which apply within the muffin tin sphere, and therefore modify the spherical part of the potential, are referred to as "non-spherical"; such corrections are those dealt with by Kleinman and Shurtleff.

Any correction to the muffin tin potential which lies outside the muffin radius can be treated exactly by the APW method, an d without much difficulty, since, just as is always the case in the OPW method, the potential in this region only appears in the form of its fourier transform. De Cicco (1967) estimated such corrections in the case of KCl and found them to be of the order of 0.01 Rydbergs. He also relates the magnitude of these corrections to the discontinuity in the potential at the muffin sphere which would be required to give suitable results if the "non-flat" contributions were not considered. However, this is only a rule of thumb and it would seem unlikely that it could be substantiated generally. Koelling (1969) considers a warped muffin tin potential and applies it to the diamond structured grey tin, where the modification should be quite important. His potential field is an overlapping free atom potential with the usual Slater exchange contribution (see Slater, 1951); he spherically averages this potential within the

muffins, taking the full contributions outside. (N.B. Kleinman and Shurtleff (1969) have criticised such a model since, although it gives gives good results, it uses a potential which is not analytic). Koelling has found that this model produces corrections of the order of 0.1 Rydbergs in some of the energy levels. He also quotes a rather interesting estimate of the r.m.s. errors caused by assuming (a) a genuine muffin tin potential, or (b) a "non-flat" correction spherical within the muffins, the former being around 0.25 Rydbergs, the latter 0.1 Rydbergs, indicating that the "non-spherical" corrections will be rather smaller than the "non-flat" corrections included.

The next stage in the development of the potential field was to treat both "non-flat" and "non-spherical" corrections, but the latter only in a perturbative manner, justified in certain cases by estimates similar to that of Koelling quoted above. The principal work in this direction has been done by Rudge (1969) and by Kane (1971). Rudge makes a multipole expansion of the charge density inside the atomic spheres and computes the potential due to a lattice sum of multipoles by a generalised Ewald method. He calculates his radial functions from a spherical potential, but then uses the full non-spherical potential to compute the matrix elements. If the potential within the inscribed spheres is not far from spherical, and only s- and p-waves are important, this should be an adequate approximation, but the neglect of coupling terms produced by a full treatment (see below) will lead to significant errors in the transition metals. Rudge applies his method to lithium, where he finds the non-muffin tin corrections to be unimportant (typically of the order of 0.001 Rydbergs). Kane adopts a procedure very similar to that of Rudge, but concentrates on the zinc-blende lattice, applying the results to silicon. He found contributions as large as 0.22 Rydbergs due to the

non-flat part of the potential, whereas the non-spherical terms contributed at most 0.03 Rydbergs.

The paper of Kleinman and Shurtleff presents one of the most comprehensive treatments of non-spherical potentials by the APW method. They have developed formulae for the integration of the radial functions which include the non-spherical contributions to the potential, treating them exactly. They have, in order to make their method computationally practicable, also suggested a modified type of wave function which retains the plane wave form inside the atomic spheres, but adds terms which correct the low ℓ-values of the spherical harmonic expansion from spherical Bessel functions to accurate radial functions. The convergence of this method, applied to a straightforward muffin tin potential for nickel, is found to be nearly as good as with the conventional APW method, taking the expansion in spherical harmonics up to $\ell = 12$. However, the cutting down of the expansion for the wave function within the atomic spheres in this way seems hardly justified, and has not apparently been further used since this paper appeared. We shall dwell on their method here a little, however, as it will appear that the work of the following chapters may be applied to this approach in order to remove the doubtful modification of the APW basis functions, replacing the conventional form, and using symmetry properties to deal with the coupled radial equations.

We shall present here the essence of the work of Kleinman and Shurtleff, making the changes in notation necessary to cast the results into the form in which they will appear later in the present work. Their modified APW basis function can be written as

$$\chi_{\underline{k}}(\underline{r}) = (NV)^{-\frac{1}{2}}\Big\{ \exp(i\underline{k}.\underline{r}) - 4\pi \sum_{\ell}^{\text{valence}} \sum_{m} \sum_{t} \exp(i\underline{k}.\underline{R}_t) i^{\ell} Y_{\ell}^{m*}(\hat{\underline{k}}) Y_{\ell}^{m}(\hat{\underline{r}}_t) \times \left[j_{\ell}(kr_t) - R_{\ell}(r_t) j_{\ell}(kr_o)/R_{\ell}(r_o) \right] \Theta(r_o - r_t) \Big\} \qquad (1.3.4.)$$

where the Θ is a unit step function, and the vectors $\underline{R}_t$ represent lattice sites. This differs from the conventional APW basis function in that only ℓ-values corresponding to atomic valence states are summed over; the function is still continuous at the inscribed sphere, and has a discontinuous derivative, just as usual. They then use linear combinations of such basis functions in the form of variational method derived by Schlosser and Marcus (1963) for cases where two separate basis sets are used, and so derive their own secular equation, different from the standard APW expression due to the different trial functions used.

This method is then extended to a consideration of non-spherical potentials. The authors point out that to do this with the original APW method would mean the impossible job of solving (for ℓ-values up to 12) a system of 169 coupled differential equations for the new radial functions, but that their modified approach reduces this number considerably. We shall, during the course of this work, show that if their approach to the non-spherical problem is applied to the conventional APW method, then the number of coupled equations to be solved need not be unmanageably large.

Kleinman and Shurtleff assume that the crystal potential can be written in the form

$$V(\underline{r}) = \sum_{L} \alpha_L(r) X_L^{\Gamma A_1 S}(\hat{\underline{r}}) = \sum_{L} \alpha_L(r) \sum_{m} A_{L,m}^{\Gamma A_1 S} Y_{\ell}^{m}(\hat{\underline{r}}) \qquad (1.3.5.)$$

where the $X_L^{\Gamma A_1 S}(\hat{\underline{r}})$ are the symmetry adapted harmonics of the totally symmetric representation of the crystal, defined by the linear combinations

of spherical harmonics given on the right, and the L is a combined suffix representing the ℓ-value and partner index, ν (N.B. we have used the lattice harmonics of Altmann and Cracknell (1965) here, where Kleinman and Shurtleff have used the Kubic Harmonics of Von der Lage and Bethe (1947)). As we shall show in Chapter 3, the exact solution of the Schrödinger equation in such a potential can be written as

$$\psi(\underline{r}) = \sum_{\ell,m} R_\ell^m(r)\, Y_\ell^m(\hat{\underline{r}}) = \sum_{i,j} R_L^j(r)\, X_L^j(\hat{\underline{r}}) \quad , \tag{1.3.6.}$$

where the latter expansion uses the symmetry adapted harmonics of the symmetry point under consideration as the basis set. Kleinman and Shurtleff write their solution within the muffin as

$$\psi_{in}(\underline{r}) = \sum_{\nu,\ell=0}^{2} \sum_{j} R_L^j(r)\, X_L^j(\hat{\underline{r}}) + \sum_{\ell=3}^{\infty} \sum_{m} R_\ell^m(r)\, Y_\ell^m(\hat{\underline{r}}) \tag{1.3.7.}$$

since $\ell = 2$ is the highest valence ℓ-value appearing in nickel, and in their modified APW approach these $R_L^j(r)$, $\ell \leq 2$, should be the important radial functions. Inserting this solution into the Schrödinger equation with the potential of equation (1.3.6.), multiplying through by $X_L^j(\hat{\underline{r}})$ and integrating over solid angle, they obtain, converting to the units introduced in equation (2.2.1.) of Chapter 2 below

$$\left[\nabla_r^2 - \frac{\ell(\ell+1)}{r^2} + 2\alpha_0(r) + 2 B_2^j \delta_{j,\ell}\, \alpha_4(r) + \epsilon \right] R_L^j(r)$$

$$= -2 \sum_{\ell'=3}^{\infty} \sum_{m'} \sum_{\nu',\ell'=4}^{\infty} \alpha_{L''}(r)\; {}^{o}R_{\ell'}^{m'}(r) \int X_L^j(\hat{\underline{r}})\, X_{L''}^{\nu' m'}(\hat{\underline{r}})\, Y_{\ell''}^{m''}(\hat{\underline{r}})\, d\Omega \,, \tag{1.3.8.}$$

where the zero superscript on the ${}^{o}R_\ell^m(r)$ indicates that this is from the previous iteration. (The actual radial equation arising when the wave function of equation (1.3.6.) and potential of equation (1.3.7.) are inserted into the Schrödinger equation is derived in Section 3.5. of Chapter 3 of this thesis, and may be written in similar form to equation

(1.3.8.), though without the zero superscript on the radial functions on the right. The use of the iterative technique proposed by Kleinman and Shurtleff is founded on their observation that the terms on the right will be small - see below, so that taking radial functions on the right from the previous iteration should, whilst simplifying the solution of the equations, provide a reasonably convergent approach). Since the lowest non-zero harmonic in the cubic potential expansion is $\ell = 4$, the the only mixing of the valence states $\ell = 0,1,2$ is $\ell = 2$ with $\ell = 2$ (this statement is associated with the properties of the Wigner 3-j symbols which will be discussed in detail in Chapter 3). The use of the symmetry adapted representation here uncouples this mixing and the left hand side of equation (1.3.8.) contains only a single valence $R_\ell^j(r)$. The right hand side contains all the non-valence ${}^oR_\ell^m(r)$, and since these are expected to be small compared to the valence radial functions, the iterative process should converge rapidly. The coefficient B_2^j introduced in equation (1.3.8.) is given by

$$B_2^j = \int [X_2^j(\hat{r})]^2 X_4^{\Gamma_{A_{1g}}}(\hat{r}) d\Omega \quad . \qquad (1.3.9.)$$

The equation (1.3.8.) is exactly analogous to those we shall derive in Chapter 3, though we do not mix radial functions in the symmetry adapted representation, $R_L^j(r)$, with the general functions $R_\ell^m(r)$ in the same equation. The iterative method of solution proposed by Kleinman and Shurtleff will also prove useful in the work of Chapter 4.

Having obtained the required radial functions, the variational procedure is undertaken in the same way as described above in the spherical case, but with more complicated matrix elements arising due to the m-dependence of the radial functions. These matrix elements

are written out by Kleinman and Shurtleff, and they will not be reproduced here.

The latest developments of the APW method in its application to non-spherical potentials are embodied in the work of Evans and Keller (1971) and of John, Lehmann and Zeische (1972), each of whom considers the treatment of such potentials within the muffin tin sphere, applying their work to both the KKR and APW methods. As the APW work is more closely related to our own, it is this part of the work which will be discussed here; also, their KKR approach seems to have been superseded by the comprehensive treatment of Williams and Morgan (1974) to be discussed in the following section. We shall once again convert their units and notation to be consistent with our own in the work which follows.

Evans and Keller consider the general problem of a non-spherical potential given by

$$V(\underline{r}) = V(r) + \sum_{L''} \alpha_{L''}(r)\, Y_{L''}(\hat{\underline{r}}) \quad , \qquad (1.3.10.)$$

where we again use the L as a combined suffix, this time representing ℓ-value and m-value. The Schrödinger equation, in the units of Chapter 2,

$$\left[\nabla^2 + 2V(\underline{r}) + \epsilon\right] \psi_{\underline{k}}(\underline{r}) = 0 \qquad (1.3.11.)$$

then has solutions of the form

$$\psi_{\underline{k}}(\underline{r}) = \sum_{L'} \phi^{\underline{k}}_{L'}(r)\, Y_{L'}(\hat{\underline{r}}) \quad , \qquad (1.3.12.)$$

where

$$\left[\nabla_r^2 - \frac{\ell(\ell+1)}{r^2} + \epsilon + 2V(r)\right] \phi^{\underline{k}}_{L}(r) = \sum_{L'} a_{LL'}(r)\, \phi^{\underline{k}}_{L'}(r) \quad , \qquad (1.3.13.)$$

and

$$a_{LL'}(r) = -2 \sum_{L''>0} \alpha_{L''}(r) \int Y^*_{L}(\hat{\underline{r}})\, Y_{L'}(\hat{\underline{r}})\, Y_{L''}(\hat{\underline{r}})\, d\Omega \qquad (1.3.14.)$$

This analysis will be presented in more detail in Chapter 3. The radial functions $\phi_L^k(r)$ contain the superscript $\underline{k}$ to indicate that, in the context of scattering theory, scattering from a non-spherical potential will clearly depend on the direction of incidence of the electron wave. Evans and Keller then construct APW's

$$\chi_{\underline{k}}(\underline{r}) = \begin{cases} \exp(i\,\underline{k}\cdot\underline{r}) \quad , & r > r_i \\ \sum_L i^\ell\, a_L^k\, \phi_L^k(r)\, Y_L(\hat{\underline{r}}) \quad , & r \leq r_i \quad , \end{cases} \tag{1.3.15.}$$

which are not in general solutions of the Schrödinger equation within the muffin tin sphere, since the individual terms $\left[\phi_L^k(r) Y_L(\hat{\underline{r}})\right]$ are not solutions. This fact leads to an extra term in the secular equation for the variational energy corresponding to the inequality

$$\int_{\substack{\text{muffin tin} \\ \text{sphere}}} \Psi_{\underline{k}}^*(\underline{r}) \left[\nabla^2 + 2V(\underline{r}) + \epsilon\right] \Psi_{\underline{k}}(\underline{r})\, d\tau \neq 0 \quad , \tag{1.3.16.}$$

for trial functions of the form

$$\Psi_{\underline{k}}(\underline{r}) = \sum_{\underline{g}} \alpha_{\underline{k}-\underline{g}}\, \chi_{\underline{k}-\underline{g}}(\underline{r}) \quad , \tag{1.3.17.}$$

where $\underline{g}$ is a reciprocal lattice vector.

To solve the radial equation (1.3.13.), Evans and Keller employ the method of Boardman, Hill and Sampanthar (1967), constructing $(\ell_{max} + 1)$ linearly independent sets of solutions of the equations, labelled $q_L^i(r)$, by using this number of different initial boundary conditions, so that the true solutions are given by

$$\phi_L^k(r) = \sum_i D_i^k\, q_L^i(r) \quad , \tag{1.3.18.}$$

where D_i^k are constants to be determined. John, Lehmann and Zeische have covered similar ground in their work, though in what seems to be a much

more convenient representation. They remove the need to solve equation (1.3.13.) for $(\ell_{max} + 1)^2$ different sets of boundary conditions by introducing at the start a further pair of angular momentum quantum numbers, and taking

$$\phi_L(\underline{r}) = \sum_{L'} Y_{L'}(\hat{\underline{r}})\, \mathcal{R}_{L'L}(r) \qquad (1.3.19.)$$

as a set of solutions within the muffin tin sphere. (See Section 4.3. below for a further discussion of this step.). The functions $\mathcal{R}_{L'L}(r)$ correspond to the $\phi^{k}_{L}(r)$ of Evans and Keller, the L' taking the place of the i in their g^{i}_{L}. The convenience of this representation soon becomes apparent, for the APW's are now written

$$\chi_{\underline{k}}(\underline{r}) = \begin{cases} \exp(i\underline{k}.\underline{r}) \;, & r > r_i \\ \sum_{L} i^{\ell} a^{k}_{L} \sum_{L'} Y_{L'}(\hat{\underline{r}})\, \mathcal{R}_{L'L}(r) \;, & r \leqslant r_i, \end{cases} \qquad (1.3.20.)$$

and it is clear that these functions are now solutions of the Schrödinger equation within the muffin tin sphere, and therefore that no extra term is produced in the secular equation for the variational energy.

We shall adopt the form of solution given in equation (1.3.19.) in Chapter 4 in the case of the Cellular Method, though the form will be proposed for the whole range of r out to the Wigner-Seitz cell boundary. We shall also show formally how the extra quantum number can be introduced to eliminate the dependence of the solutions on the initial conditions used, thus linking the form of Evans and Keller with that of John et al. The use of a form of trial function which does not satisfy the Schrödinger equation is not convenient in the Cellular Method, due to the non-standard way in which the variational method is treated; this will be pointed out in the Appendix to Chapter 4, where the approach is attempted.

In this section we have summarised the work done in the APW field on the treatment of the non-spherical potentials, presenting details of the techniques used in the work which will be followed in the approaches adopted in the forthcoming chapters. In the next section we move on to deal with the KKR method in a similar context.

1.4. The KKR, or Green's Function Method.

Green's function techniques, since their development by Korringa (1947) and by Kohn and Rostocker (1954) have appeared in many different, but basically equivalent formulations, ranging from the multiple scattering formulation to an approach equivalent to that of the APW method. Ham and Segall (1961) first took up the method and produced results for the calculations of energy bands of the alkali metals (Ham, 1962), aluminium (Segall, 1961) and the noble metals (Segall, 1962) which at once established the method as one of the best methods of calculating band structures. The review of Segall and Ham (1968) brings the treatment of muffin tin potentials, on which the method relied for its simplicity, up to date although perhaps making light of the need to move away from the muffin tin approximation.

As mentioned in connection with the APW method, Beleznay and Lawrence (1968) have shown how the KKR method can be easily adapted to treat a potential non-flat in the region outside the muffin tin spheres. If the KKR approach is formulated in the reciprocal lattice representation, as developed by Ziman (1965), then the correction is once again, as in the APW method, shown to have the very simple effect of adding to each matrix element the corresponding Fourier component of a potential equal to the

interstitial potential outside the muffin tin sphere, and zero inside.

We shall first introduce the essential details of the KKR approach, before moving on to discuss the work of Williams and Morgan (1974) on general potentials. The formal solution of the one electron Schrödinger equation, for energy ϵ, written in the form

$$\left[\nabla^2 + \epsilon\right]\psi(\underline{r}) = V(\underline{r})\,\psi(\underline{r}) \,, \tag{1.4.1.}$$

is given by

$$\psi(\underline{r}) = \int_{\text{unit cell}} G(\underline{r},\underline{r}')\,V(\underline{r}')\,\psi(\underline{r}')\,d\underline{r}' \,, \tag{1.4.2.}$$

where $\psi(\underline{r})$ satisfies the usual Bloch condition and $G(\underline{r},\underline{r}')$ satisfies the equation

$$\left[\nabla^2 + \epsilon\right] G(\underline{r},\underline{r}') = \delta(\underline{r}-\underline{r}') \,. \tag{1.4.3.}$$

Dividing the integral into two parts, one within the muffin tin sphere, $(r \leqslant r_o)$, the other outside, and transforming the former to a surface integral by Green's theorem, we obtain

$$\int_{r'=r_o} \left\{ G(\underline{r},\underline{r}')\frac{\partial}{\partial r'}\psi(\underline{r}') - \psi(\underline{r}')\frac{\partial}{\partial r'} G(\underline{r},\underline{r}') \right\} dS' + \int_{r>r_o} G(\underline{r},\underline{r}')\,V(\underline{r}')\,\psi(\underline{r}')\,d\underline{r}' = \begin{cases} \psi(\underline{r}) \,, & r > r_o \\ 0 \,, & \text{otherwise} \end{cases} \tag{1.4.4.}$$

Next expand the unknown wave function in solutions of the radial equation as

$$\psi(\underline{r}) = \sum_L i^l R_l(r)\,Y_L(\hat{\underline{r}})\,a_L \,. \tag{1.4.5.}$$

We also require the expansion of $G(\underline{r},\underline{r}')$ in spherical harmonics. It can

be shown (see Ziman, 1971) that we can write

$$G(\underline{r},\underline{r}') = K \sum_L j_l(Kr)\{n_l(Kr') - i j_l(Kr')\} Y_L(\hat{r}) Y_L(\hat{r}') \qquad (1.4.6.)$$

$$+ \sum_L \sum_{L'} i^{l-l'} B_{LL'} j_l(Kr) j_{l'}(Kr') Y_L(\hat{r}) Y_{L'}(\hat{r}') ,$$

where $K^2 = \epsilon$, and the coefficients $B_{LL'}$ can be shown to depend only on the structure of the crystal concerned. Using equations (1.4.5.) and (1.4.6.) in the variational condition, equation (1.4.4.) leads to the required secular determinant, which is similar in form to that of the APW method.

Boardman, Hill and Sampanthar (1967) were amongst the first to consider multiple scattering from non-spherically symmetric potentials. The radial equations which they produced are almost identical to those of the present work, though they apply theirs to cases where there is an axis of symmetry in the problem, thus simplifying greatly the coupling coefficients which we discuss in Chapter 3. Evans and Keller follow up this work, as well as treating the APW method in the way outlined above, still retaining the muffin tin spheres, though considering the insertion of extra spheres into the model, centred between the lattice sites. This technique is given a firm grounding by the work of Williams and Morgan (1974) who go further in removing the muffin tin spheres altogether, and considering merely a cellular potential. Their work seems to be the biggest step forward in the treatment of non-spherical potentials to date, and we shall pause here to consider some important details of their work.

Williams and Morgan treat the KKR method as an application of the more general multiple scattering theory, and it is in this formulation that the work can be approached. However our task here will be to pick out the essential details of their approach without going into

the depths of the formalism. They require only that we deal with scatterers which do not intersect, and this is most conveniently done by dividing the lattice up into cells, with the cellular potentials, $v_\mu(\underline{r} - \underline{R}_\mu)$ for a cell centred at $\underline{R}_\mu$, defined to be zero outside that cell. These cellular potentials combine to give a total scattering potential

$$V(\underline{r}) = \sum_\mu v_\mu(\underline{r} - \underline{R}_\mu) , \qquad (1.4.7.)$$

and the equation (1.4.2.) for the wave function rewritten in the form

$$\psi(\underline{r}+\underline{R}_\mu) - \int G(\underline{r}-\underline{r}')\, v_\mu(\underline{r}')\, \psi(\underline{r}'+\underline{R}_\mu)\, d\underline{r}' = \sum_{\mu \neq \mu'} \int G(\underline{r}-\underline{r}'+\underline{R}_{\mu\mu'})\, v_{\mu'}(\underline{r}')\, \psi(\underline{r}'+\underline{R}_{\mu'})\, d\underline{r}' , \qquad (1.4.8.)$$

where $\underline{R}_{\mu\mu'} = \underline{R}_\mu - \underline{R}_{\mu'}$, and the $\mu = \mu'$ term in the summation has been taken over to the left of the equation. The wave function in each cell is expanded as a linear combination of functions which are solutions of the Schrödinger equation containing only the cellular potential $v_\mu(\underline{r})$, viz.

$$\psi(\underline{r}+\underline{R}_\mu) = \sum_{L'} \gamma^\mu_{L'}\, \phi^\mu_{L'}(\underline{r}) . \qquad (1.4.9.)$$

They then proceed to define the functions $\phi^\mu_{L'}(\underline{r})$ in terms of sets of phase constants, but in principle it is still possible to obtain the $\phi^\mu_{L'}(\underline{r})$ directly from the Schrödinger equation , where the solutions are of the form given in equation (1.3.19.). Assuming this done, we return to equation (1.4.8.), which must now be dealt with as it stands as there is no convenient muffin tin sphere over which to perform the equivalent surface integral, as done in equation (1.4.4.) for the muffin tin approximation. We require an expansion for the free particle propagator, and under certain circumstances the following expansion is valid:

$$G(\underline{r}-\underline{r}'+\underline{R}_{\mu\mu'}) = \sum_{L,L'} \left(\frac{i}{\kappa}\right)^{\ell} j_\ell(\kappa r)\, Y_L(\hat{\underline{r}})\, G'_{LL'}(\underline{R}_{\mu\mu'}) \left(\frac{-i}{\kappa}\right)^{\ell'} j_{\ell'}(\kappa r')\, Y^*_{L'}(\hat{\underline{r}}') , \qquad (1.4.10.)$$

where $\kappa^2 = \epsilon$, and the $G'_{LL'}(\underline{R}_{\mu\mu'})$ are the structure constants of multiple scattering theory defined so that $G'_{LL'}(0)$ is zero. The conditions of

validity of the above expansion are shown by Williams and Morgan to be such that the inequalities

$$r' < |\underline{R}_{\mu\mu'} + \underline{r}| \quad \text{and} \quad r < R_{\mu\mu'} \qquad (1.4.11.)$$

$$r < |\underline{R}_{\mu\mu'} - \underline{r}'| \quad \text{and} \quad r' < R_{\mu\mu'}$$

must both be violated if the expansion is to be invalid. The validity cannot be proved for the diamond and zinc blende lattices, but they point out that by partitioning space into cells half of which are centred in the large open regions of the structures, the conditions can be satisfied for these structures also. (This ties up with the work of Keller (1971), referred to above). The validity of the expansion (1.4.10.) removes the necessity for the muffin tin potential approximation, and using this in equation (1.4.8.) along with equation (1.4.9.) and an expression like equation (1.3.19.) the problem is in principle solved, though, as pointed out above, Williams and Morgan approach the solution in a different manner.

In proposing their approach to the problem, they raise two questions which only extensive numerical calculations will answer - these are concerned with (i) the capability of the technique to deal with covalently bonded systems in which the potential and wave functions are often better described as centred between rather than at the atomic nuclei, and (ii) possible difficulties arising due to the abrupt truncation of the potential at the cell surfaces. Similar problems will arise in the approaches we shall use, and once again only time, and many different numerical calculations will answer the questions. The importance of the work of Williams and Morgan lies in the removal of the Muffin tin spheres from the calculations, a concept which has never been required in the Cellular Method and which will be discussed in the following section.

1.5. The Cellular Method

Chapter 2 will present a resumé of the Cellular Method, and we shall, therefore, in this section only attempt to put the method in its place amongst the methods described in the previous sections of this chapter, and to indicate the advantages of a treatment of non-spherical potentials in the formulation of the Cellular Method.

Unlike the methods of band structure calculation discussed above, the Cellular Method has little in the way of a precise physical basis. The KKR method quite clearly considers the electrons as particles moving in a lattice of scatterers, and uses scattering theory as the basis of its formulation; the APW method considers the physically justifiable model of a spherical potential around each atom, where the wave function may be written in terms of spherical wave functions, and outer regions where the electrons are nearly free and are described by plane waves, which must be continuous with the spherical wave functions at the boundary of the spherical region; the OPW method takes plane waves throughout, orthogonalising them to atomic wave functions, again a physically sound procedure. The Cellular Method, on the other hand, merely calculates the wave functions in any given unit cell by solving the Schrödinger equation for the given potential and matching the solutions to the Bloch condition on the cell surface in a Monte Carlo fashion; the physical concepts are embodied only in the potential field used. This does not, however, prevent the method from being at least as accurate as the other methods mentioned (see, for instance Connolly, 1971), and it will be shown during the course of this work that the method is both physically suited, and easily adapted to the treatment of non-spherical potentials. The clear advantage of the KKR method is that it is applicable to non-periodic systems, but in the domain of periodic structures the Cellular

Method is almost certainly the easiest to compute, in all but the simplest cases.

In applying the Cellular Method to non-spherical potentials, our main concern will be that we retain the convergence of the cellular expansion. Convergence has been discussed in detail by Altmann (1974), who shows that, although only analytically proved for certain restricted classes of muffin tin potential (see Section 2.4. of Chapter 2), the method converges well even when a full cellular potential, varying with radius r over the whole cell, is used. Therefore, although checks on the convergence of the expansion will be necessary in all the work which follows, we are confident that the use of non-spherical, full cellular, potentials will not prove to be the downfall of the method. Having established this point there will be no further need to rely on the muffin tin potential approximation, and we require only a potential defined through the whole Wigner-Seitz cell.

In moving from a spherical potential to one with the full symmetry of the lattice, it does not seem appropriate to introduce spheres as boundaries in any part of the problem, and as it is the Wigner-Seitz cell which reflects the lattice symmetry, the matching of the boundary conditions on the cell surface appears to be a physically acceptable approach. This is in contrast to the APW method, where a sphere must be introduced on which to match plane wave and interior functions, and where furthermore the treatment of a non-spherical potential must be considered in two parts (see Section 1.3. above) as the "non-flat" and "non-spherical" corrections respectively. A similar criticism may be levelled at the non-spherical adaption of the KKR method in all but the formalism proposed by Williams and Morgan, who recognise the need to move away from the muffin tin

approximation. In short, if non-spherical potentials are used, the muffin tin either remains as a very artificial concept, or is abandoned. The potential over the full cell has to be introduced. The Cellular Method is the only one which, right from the start, has treated the potential over the full cell, and it is for this reason that it appears more natural, and therefore more economical to introduce non-spherical terms into the method. The treatment of non-spherical potentials by the Cellular Method is therefore a technique which could be usefully developed and tested, and it is to this end that the work which follows has been undertaken.

The techniques to be developed will be valid for any non-spherical potential, and indeed are at present being used in this department by C. P. Mallett (private communication) for a study of the graphite lattice, where the non-spherical terms are very large. For purposes of testing the theory, however, a somewhat limited case of a non-spherical potential for copper was chosen, and this was done for two reasons. The first is a numerical one, namely that in the case chosen one had some guidance as to the expected order of magnitude of the non-spherical corrections which thus provided a test on the numerical side of the program. The second reason is more involved and has a partly historical character. In the standard form of the Cellular Method, the potential outside the unit cell is doctored in order to create a spherical symmetry around the centre of the first unit cell. This merely involves assuming the spherical extension of the potential within the whole of the cell's circumscribing sphere. A glance at Figure 3.3.1 of Chapter 3, drawn for the hypothetical two dimensional square lattice, will convince us that the

points of the circle of radius r shown may be in the first unit cell, centred at O , or in one of the neighbouring cells, and would therefore be at different potentials, despite being the same distance from O . The above assumption neglects this point. The problem will arise for $r_i < r < r_c$, and might thus be expected to affect the wave functions on the Wigner-Seitz cell surface, required by the Cellular Method.

The justification of this procedure, and therefore of the spherical form of the Cellular Method, is based on the fact that the solution of the Schrödinger equation is fully determined by the values of the wave function and derivative on the cell boundary, and therefore that the results are independent of any arbitrary extension of the potential outside the cell. Therefore, the two series which correspond to the spherical and non-spherical solutions respectively should converge to the same limit. This result, however, is only of theoretical interest since there is no reason why the truncated series, that must in practice be substituted for the infinite one, should give the same answer for the same value of ℓ (ℓ_{max} , say) at which the series are truncated. In other words, there are no grounds to postulate the same rate of convergence for both expansions.

For the above reason, the spherical form of the Cellular Method was alleged for many years to lack the necessary guarantees of convergence when used, of course, with truncated expansions. Saffren (1959) pointed this out, and this work was independently done by Ham (1954). Both authors claimed that the spherical Cellular Method contains non-spherical truncation errors when muffin tin potentials are used with radius greater than $(2 r_i - r_c)$. For then the circumscribing sphere of one cell will intersect the muffin tin spheres of neighbouring cells, thus producing non-spherical parts to the potential about the central

cell in the outer regions of the circumscribing sphere. Altmann (1974) has reproduced in full the analysis of Saffren, and it is not intended to reiterate his work here.

These allegations of lack of convergence of the Cellular Method in its spherical form have continually been repeated in the literature. Thus Dimmock (1971) says "The cellular wavefunctions will not converge to the true wavefunction solutions of the periodic potential problem except within a sphere inscribed in the Wigner-Seitz cell. Outside that sphere, some other form of the expansion must be used." He does not mention here that the statement is valid only for potentials with muffin radius greater than the value of $(2 r_i - r_c)$, as discussed above. Further statements have been made, as for example when Altmann et al. (1968) obtained agreement with the results of Burdick (1963) for copper calculated by the APW method, the agreement being to within 0.002 Rydbergs, Anderson and Fricker (1971) claimed that the results had no general validity since "even for a periodic muffin tin potential one has in general no a priori knowledge that [the spherical cellular expansion] converges outside the inscribed sphere". In a private communication they qualified this statement for a muffin radius larger than $(2 r_i - r_c)$, in line with the work of Saffren and of Ham.

It is for these reasons that it was considered necessary to test to what extent the results of the spherical Cellular Method differ from those obtained when Saffren's non-spherical corrections are taken into account. Since such corrections apply only for $r_i < r < r_c$, the application provides a convenient means of testing the non-spherical theories developed without becoming involved in heavy computational problems.

The potential of Chodorow as employed by Burdick (1963) for his calculation of the band structure of copper is chosen as a basis for our investigation of the non-spherical correction to the Cellular Method. Copper has been a popular choice for work on band structure calculations, having the following virtues: it is of F.c.c. structure, making the muffin tin approximation quite useful, is non-magnetic, is light and therefore relativistic effects are not important, and most important, de Haas van Alphen and optical data of high precision is available for comparison. The uncorrected Cellular Method has produced results in good agreement with those of Burdick (see Altmann et al., 1968) which are in turn consistent with those of other workers using this, and other potentials (for instance Ballinger and Marshall, 1967), so that we should expect the non-spherical corrections in this case to be much smaller than those quoted in Section 1.3. above. A full discussion of the potential employed is presented in Section 6.2. of Chapter 6.

1.6. A Plan of the Thesis.

Chapter 2 will provide the necessary grounding for the new work to follow. The calculation of radial functions in the case of a spherical potential is considered so that the step up to an examination of non-spherical potentials can be presented in these terms. The use of symmetry adapted harmonics in the expansion of the crystal wave function is considered, in order to give sufficient grounding in the group representation theory required in Chapters 3 and 4. Finally a brief account of the Cellular Method is presented, laying special emphasis on the parts of the technique which must be changed when the more complicated wave functions of the

non-spherical case are considered.

In Chapter 3 we first calculate the full non-spherical potential resulting from a superposition of atomic potentials, using the method of Mattheiss (1964 a) as presented by Loucks (1967), but including also the nonspherical terms, which they do not. An expansion of the potential in spherical harmonics is obtained for the f.c.c. lattice. Following on from this we calculate the non-spherical correction to the muffin tin approximation required for its correct use in the Cellular Method, as described in the previous section, obtaining a form similar to that for the general non-spherical potential. We next consider the effect of such forms of potential on the Schrödinger equation, deriving the new form of radial function and the set of coupled equations by which they are given. The final sections of the chapter are devoted to a consideration of the properties of the coupling coefficients from these radial equations, both in the general case and in the cases where it is useful to have the radial functions in symmetry adapted representation.

Chapter 4 considers in detail the wave functions of the non-spherical case. The form of the new radial functions is considered, and methods of solution of the radial equations proposed. The full treatment proposed involves a wave function of differen t form from the spherical case, and therefore the Cellular Method must be adapted to deal with such differences; the necessary changes are developed.

Chapter 5 describes the computer programs written to obtain band energies in the case of the corrections to the muffin tin approximation. The emphasis is on the new programs for the coupling coefficients, and the cellular (MASTER) program which has required substantial revision.

Finally, Chapter 6 presents the results of calculations performed on the corrections to the muffin tin approximation in the Cellular Method for the f.c.c. structured copper, using the muffin tin potential of Chodorow (1939) as employed by Burdick (1963). The results are presented for the variety of methods developed in Chapter 4, and these various methods are assessed. A discussion of the work in relation to that discussed earlier in the present chapter, together with indications of the directions in which this work is at present being extended bring the thesis to a close.

CHAPTER 2

RADIAL FUNCTIONS, SYMMETRISATION AND THE CELLULAR METHOD

2.1. Introduction.

This chapter is concerned with the basic solution of the Schrödinger equation in a crystal lattice in order to produce, ultimately, the electronic energy band structure of a crystalline solid. As stated in the previous chapter, the work on non-spherical potentials requires substantial changes to the radial wave functions, both in form, and in method of calculation. It will also prove useful to use radial wave functions in a symmetry adapted representation, and therefore a knowledge of the symmetry adapted harmonics and their method of generation will be important. These harmonics have been calculated for the cubic groups by Altmann and Cracknell (1965), and for asymmorphic space groups by Altmann and Bradley (1965); in order to retain uniformity with the applications required, the work here will be concerned with the cubic groups. It has also been pointed out in the previous chapter that the crystal wave function is of a different form in the non-spherical case, so that the formation of the boundary condition matrix and its manipulation require a different treatment, and therefore we shall present the methods used in the spherical case here for reference.

A comprehensive review of the Cellular Method, and all the techniques which it involves is given by Altmann (1974), and it is not intended to reproduce such an account here. We shall merely attempt to provide a thorough grounding in the areas which require modification or extension when the non-spherical case is treated in the later chapters of this work.

2.2. The Radial Equation and its Solution.

The Schrödinger equation for the wave functions within a unit cell of a crystal lattice, written with the energy, ϵ in Rydbergs, and the potential in negative atomic units (see Altmann, 1974) is written

$$\nabla^2\phi(\underline{r}) + 2\left[V(\underline{r}) + \tfrac{1}{2}\epsilon\right]\phi(\underline{r}) = 0 \qquad (2.2.1.)$$

In the case of a spherically symmetric potential, for which

$$V(\underline{r}) = V(r) \quad , \qquad (2.2.2.)$$

it is well known that the wave functions are separable into radial and angular parts, and are of the form

$$\phi_{\ell m}(\underline{r}) = R_\ell(r)\, Y_\ell^m(\hat{\underline{r}}) \qquad (2.2.3.)$$

where the angular momentum quantum numbers ℓ and m are integral with $\ell \geq 0$ and $|m| \leq \ell$, and the $\hat{\underline{r}}$ refers to the angular coordinates θ and ϕ . The $Y_\ell^m(\hat{\underline{r}})$ are the well known spherical harmonics (see, for example, Edmonds, 1960), and the $R_\ell(r)$ are radial functions given by the equation (2.2.5.) below. On substituting equation (2.2.3.) into the Schrödinger equation (2.2.1.), and employing the spherical polar form of the operator ∇^2 together with the defining equation for the spherical harmonics,

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = -\ell(\ell+1)Y \quad , \qquad (2.2.4.)$$

we obtain

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_\ell(r)}{dr}\right) - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right]R_\ell(r) = 0 \, . \qquad (2.2.5.)$$

This equation must be solved numerically for a given potential to give the radial functions for all ℓ-values required, at each given energy, ϵ .

Altmann (1974) has shown that these radial functions must be known to eight significant figures in order to obtain the required accuracy in the cellular calculations, so that some care must be taken over the choice of a suitable method for the integration of equation (2.2.5.).

The substitutions

$$\rho = \ln(r) \qquad (2.2.6.)$$

and

$$G_\ell(\rho) = R_\ell(r) \exp(\tfrac{1}{2}\rho) \qquad (2.2.7.)$$

cast equation (2.2.5.) into the form

$$\frac{d^2G_\ell(\rho)}{d\rho^2} + \left\{\left[\epsilon + 2V(\rho)\right]\exp(2\rho) - (\ell+\tfrac{1}{2})^2\right\} G_\ell(\rho) = 0, \qquad (2.2.8.)$$

which contains no first derivative and can be integrated by the method of Numerov (see Hartree, 1958). This method is adequate provided that the potential, $V(\rho)$, does not vary too quickly, and is therefore suitable except in the central regions of the Wigner-Seitz cell. In order to solve the equation in these inner regions another technique must be found; the transformation

$$H_\ell(\rho) = G_\ell(\rho) \exp\{-(\ell+\tfrac{1}{2})\rho\} \qquad (2.2.9.)$$

is applied to equation (2.2.9.), leading to the pair of simultaneous first order differential equations

$$\frac{dG_\ell(\rho)}{d\rho} = -(2\ell+1)\,Q_\ell(\rho) - \left\{2V(\rho)+\epsilon\right\} H_\ell(\rho)\exp(2\rho), \qquad (2.2.10.)$$

where

$$\frac{dH_\ell(\rho)}{d\rho} = Q_\ell(\rho), \qquad (2.2.11.)$$

which are integrable by the Runge Kutta method (Gill, 1951). Starting values

for this integration are obtained by making series approximations to $V(\rho)$, $H_l(\rho)$ and $Q_l(\rho)$ near the origin, and the integrations are done step by step on the grid

$$\rho = -6.125 + j/64 \quad , \quad j = 0,1,2,\ldots \qquad (2.2.12.)$$

The radial functions thus obtained must be normalised, and this is usually done over the volume of the equivalent sphere of radius r_e ($= \exp \rho_e$), that is the sphere centred at the centre of the Wigner-Seitz cell, and with volume equal to that of the cell. We therefore require the value of the normalisation constant N_l given by

$$N_l^2 = \int_0^{r_e} R_l^2(r)\, r^2\, dr \quad . \qquad (2.2.13.)$$

The numerical details of all the above integrations will be referred to in Chapter 5, along with the computational details.

For the sake of completeness, it is convenient to mention here an alternative method of obtaining the normalisation constant when the Runge Kutta procedure has been used over the whole radial grid (as is the case in methods adopted for the non-spherical case). For then, regarding H_l in equation (2.2.13.) as a function of r_e, we may rewrite this equation in differential form as

$$\frac{dN_l^2(r_e)}{dr_e} = R_l^2(r_e)\, r_e^2 \quad , \qquad (2.2.14.)$$

which, with the transformations of equations (2.2.6.), (2.2.7.) and (2.2.9.) becomes

$$\frac{dN_l^2(\rho)}{d\rho} = H_l^2(\rho) \exp\{(2l+3)\rho\} \quad , \qquad (2.2.15.)$$

and which may be solved along with equations (2.2.10.) and (2.2.11.), step by

step, in the Runge Kutta routine, the value of $N_\ell^2(\rho_e)$ being interpolated from the surrounding values on the radial grid.

Finally the derivatives of the normalised radial functions are required over the region of the cell boundary. If the Numerov integration has been used in the outer regions, these must be calculated directly using a six point difference method to differentiate the $R_\ell(r)$ (see Hartree, 1958), whereas if the Runge Kutta method has been used throughout, then no further differentiation is required, since

$$\frac{dR_\ell(r)}{dr} = \frac{dR_\ell}{d\rho}\frac{d\rho}{dr} = e^{\rho}\frac{d}{d\rho}\left[P_\ell(\rho)\exp(\ell\rho)\right]$$

$$= \left\{Q_\ell(\rho) + \ell P_\ell(\rho)\right\}\exp\left[(\ell-1)\rho\right] . \qquad (2.2.16.)$$

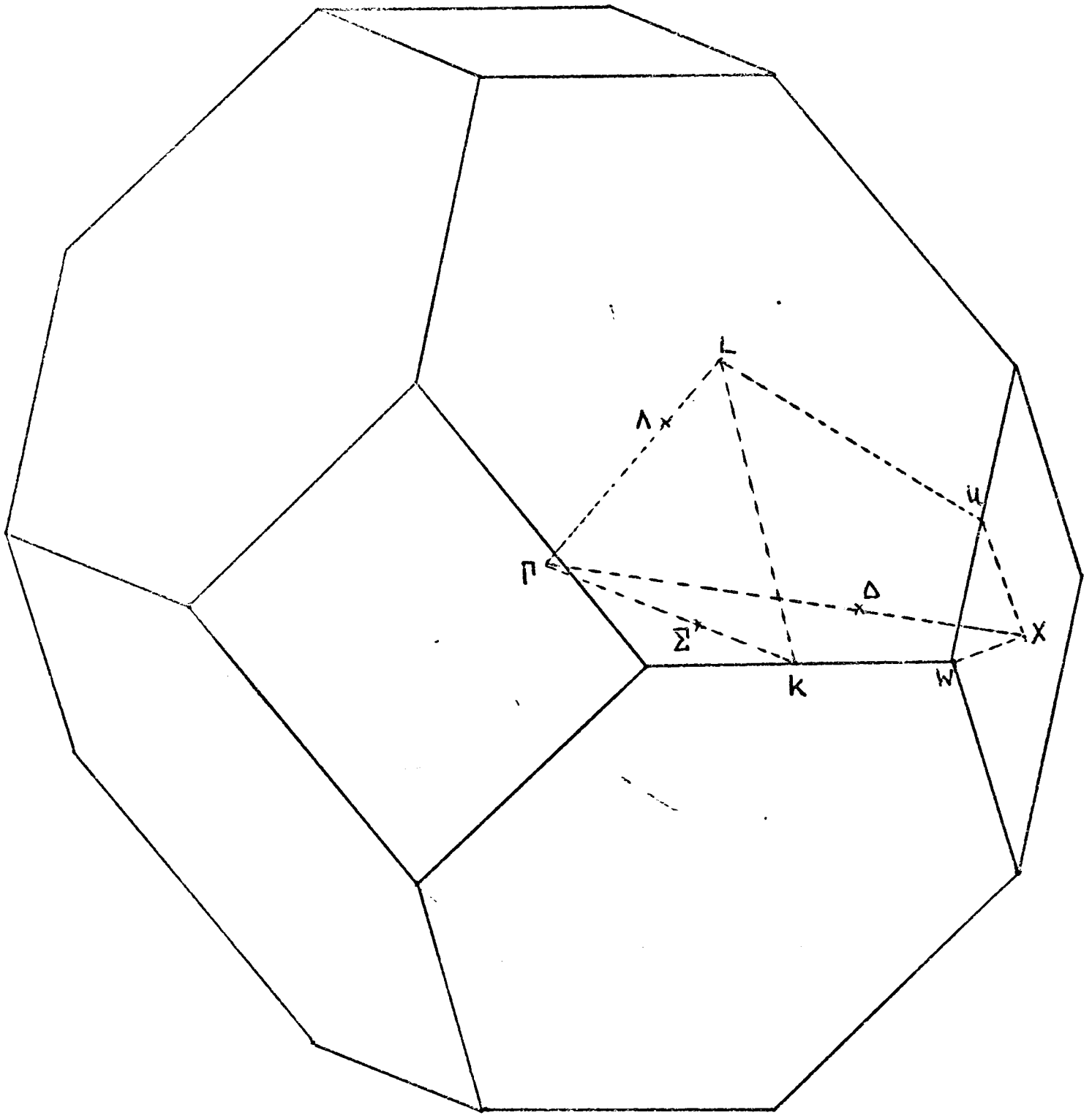
Thus the radial equation is completely solved for the given spherical potential, and the wave functions can be calculated in the form required for use in the Cellular Method to be described in Section 2.4.

2.3. The Use of Lattice Symmetry.

A brief summary of the theory used here, together with a complete set of resulting harmonics for the cubic groups is given by Altmann and Cracknell (1965), whilst an exhaustive account of the theory is presented by Bradley and Cracknell (1972).

The work is based on the Wigner projection operator method (see Wigner, 1959) given as follows. Consider a group, G, of operators, $\mathcal{R}$, with an i-th irreducible representation of matrices $\underset{\sim}{\Delta}^i(\mathcal{R})$, then on application of the projection operator

$$\sum_{\mathcal{R}\in G} \Delta^i_{ts}(\mathcal{R})^* \mathcal{R} \qquad (2.3.1.)$$



First Brillouin Zone of f.c.c. Lattice with Symmetry Points

Figure 2.3.1.

to an arbitrary function (the generator), a function symmetry adapted to the t-th column of the i-th irreducible representation of $\underset{\sim}{G}$ will be projected out. The generator will, here, always be a spherical harmonic, and the group $\underset{\sim}{G}$ will be a subgroup of the rotation operators of the symmetry group of the crystal lattice appropriate to the $\underline{k}$-vector concerned. A full account of the theory of the rotation group is given by Tinkham (1964), and we shall merely quote the necessary results here. The result of the operation of a rotation operator on a spherical harmonic is

$$\mathcal{R}\, Y_\ell^m(\hat{\underline{r}}) = \sum_n Y_\ell^n(\hat{\underline{r}})\, \mathcal{D}^\ell_{nm}(\mathcal{R}) \quad , \qquad (2.3.2.)$$

where $\underset{\sim}{\mathcal{D}}^\ell(\mathcal{R})$ is the $(2\ell + 1)$ - dimensional matrix representation of the group of operators $\mathcal{R}$, given in terms of the Euler angles α, β, γ. These matrix representatives can be written in the form

$$\mathcal{D}^\ell_{nm}(\mathcal{R}) = \exp(-im\alpha)\, d^\ell_{nm}(\beta) \exp(-in\gamma)\, C_{nm} \quad , \qquad (2.3.3.)$$

where

$$C_{nm} = i^{n+|n|}\, i^{-m-|m|} \quad . \qquad (2.3.4.)$$

Table 2.3.1. lists the Euler angles of all operations of the cubic group $\underset{\sim}{O}$, together with their matrix representatives (the operators of the full cubic group $\underset{\sim}{O}_h$ consist of these operators together with the direct product of these operators with the inversion - which just adds a factor $(-1)^\ell$ to the matrix representatives involving the inversion), as these will be required in the following chapter. A complete set of tables of the $d^\ell_{nm}(\pi/2)$ has been prepared by Bradley (1961) for ℓ-values up to 20.

We are now in a position to write down the full projection operator of Bradley and Cracknell (1972), applying it to the spherical

Table 2.3.1.

The Operations of the Cubic Group O and their Matrix Representatives

Operation	Euler Angles			Matrix Representatives
	α	β	γ	
E	0	0	0	$\delta_{n,m}$
C_{2x}	π	π	0	$e^{-i m\pi}(-1)^{\ell}\delta_{n,-m}$
C_{2y}	0	π	0	$(-1)^{\ell}\delta_{n,-m}$
C_{2z}	π	0	0	$e^{-i m\pi}\delta_{n,m}$
C_{31}^{+}	$\pi/2$	$\pi/2$	0	$C_{nm}\, e^{-i m\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{32}^{+}	$3\pi/2$	$\pi/2$	π	$C_{nm}\, e^{-3i m\pi/2}\, e^{-in\pi}\, d^{\ell}_{nm}(\pi/2)$
C_{33}^{+}	$\pi/2$	$\pi/2$	π	$C_{nm}\, e^{-i m\pi/2}\, e^{-in\pi}\, d^{\ell}_{nm}(\pi/2)$
C_{34}^{+}	$3\pi/2$	$\pi/2$	0	$C_{nm}\, e^{-3i m\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{31}^{-}	π	$\pi/2$	$\pi/2$	$C_{nm}\, e^{-i m\pi} e^{-in\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{32}^{-}	0	$\pi/2$	$3\pi/2$	$C_{nm}\, e^{-3in\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{33}^{-}	0	$\pi/2$	$\pi/2$	$C_{nm}\, e^{-in\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{34}^{-}	π	$\pi/2$	$3\pi/2$	$C_{nm}\, e^{-i m\pi} e^{-3in\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{4x}^{+}	$\pi/2$	$\pi/2$	$3\pi/2$	$C_{nm}\, e^{-3in\pi/2} e^{-i m\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{4y}^{+}	0	$\pi/2$	0	$C_{nm}\, d^{\ell}_{nm}(\pi/2)$
C_{4z}^{+}	$\pi/2$	0	0	$e^{-i m\pi/2}\delta_{n,m}$
C_{4x}^{-}	$3\pi/2$	$\pi/2$	$\pi/2$	$C_{nm}\, e^{-in\pi/2} e^{-3i m\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{4y}^{-}	π	$\pi/2$	π	$C_{nm}\, e^{-i m\pi} e^{-in\pi}\, d^{\ell}_{nm}(\pi/2)$
C_{4z}^{-}	$3\pi/2$	0	0	$e^{-3i m\pi/2}\delta_{n,m}$
C_{2a}	$\pi/2$	π	0	$(-1)^{\ell} e^{-i m\pi/2}\delta_{n,-m}$
C_{2b}	$3\pi/2$	π	0	$(-1)^{\ell} e^{-3i m\pi/2}\delta_{n,-m}$
C_{2c}	π	$\pi/2$	0	$C_{nm}\, e^{-i m\pi}\, d^{\ell}_{nm}(\pi/2)$
C_{2d}	$\pi/2$	$\pi/2$	$\pi/2$	$C_{nm}\, e^{-i m\pi/2} e^{-in\pi/2}\, d^{\ell}_{nm}(\pi/2)$
C_{2e}	0	$\pi/2$	π	$C_{nm}\, e^{-in\pi}\, d^{\ell}_{nm}(\pi/2)$
C_{2f}	$3\pi/2$	$\pi/2$	$3\pi/2$	$C_{nm}\, e^{-3i m\pi/2} e^{-3in\pi/2}\, d^{\ell}_{nm}(\pi/2)$

harmonics to obtain

$$W^{ki}_{ts}\, Y^m_\ell(\hat{r}) = \frac{l_i}{h} \sum_{R \in G^k} P_R\, \Delta^i_{ts}(R)^* \exp(-im\alpha) \sum_n C_{nm} \exp(ing) d^\ell_{nm}(\beta)\, Y^n_\ell(\hat{r}) \qquad (2.3.5.)$$

where l_i is the dimension of the i-th irreducible representation, h is the order of the group G^k, and P_R is unity when R is a proper rotation and $(-1)^\ell$ otherwise. The function so formed transforms like the t-th column of the i-th irreducible representation of the little cogroup G^k, as defined by Altmann and Cracknell (1965). Operating on some generators, W^{ki}_{ts} will automatically give zero, whilst with others, linear combinations of spherical harmonics will be produced. These linear combinations will, in some cases, when normalised, give directly the symmetry adapted harmonics of the representation concerned, whilst in other cases they will themselves be linear combinations of the symmetry adapted harmonics. In the latter case Altmann and Bradley (1963) have shown how the harmonics may be extracted from these linear combinations.

In this way the coefficients of the spherical harmonics in the expansions forming the symmetry adapted harmonics can be produced. These are coefficients presented, for cubic groups, by Altmann and Cracknell (1965), and which we shall employ in the work on non-spherical potentials presented in the later chapters. For future reference, we write equation (2.3.5.) in the form

$$X^{kj}_L(\hat{r}) = \sum_m P^{kj}_{Lm}\, Y^m_\ell(\hat{r}) \quad , \qquad (2.3.6.)$$

where j is a combined superscript representing the t-th column of the i-th irreducible representation, and L representing the ℓ-value and partner index, ν. For any symmetry point in k-space, the full set of these mutually orthogonal linear combinations, up to any maximum ℓ-value, will contain all

the possible spherical harmonics up to that ℓ-value, and must th erefore also form a complete set of functions appropriate to the chosen $\underline{k}$-vectors. We shall make use of this fact in the following chapters.

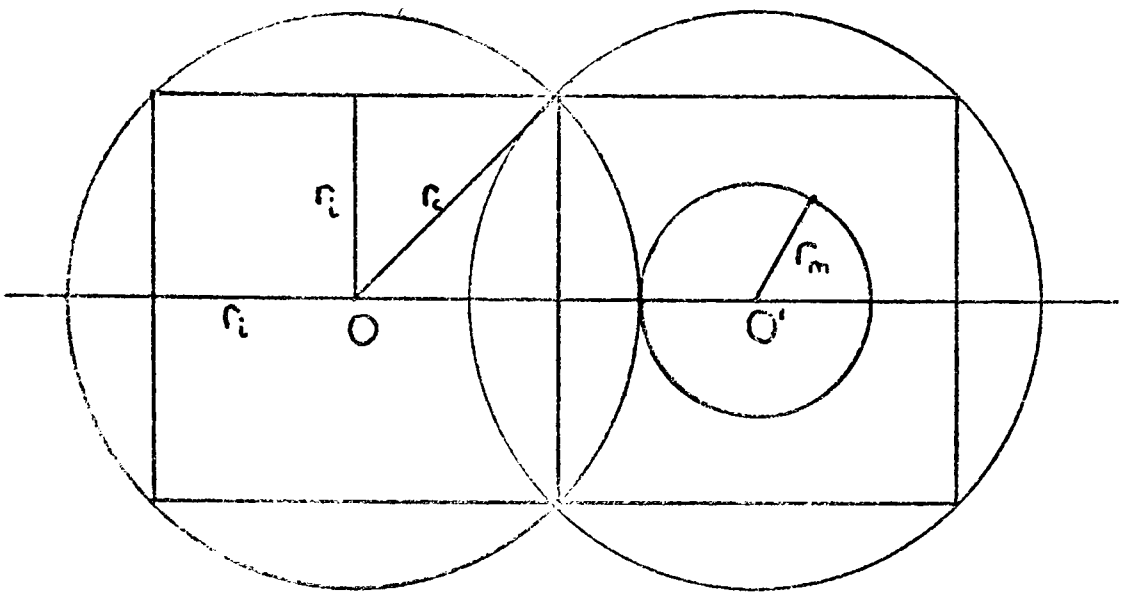
2.4. The Cellular Method.

This section will provide a resumé of the Cellular Method, concentrating on the sections which will require modification in the non-spherical case, together with a discussion of the convergence of the cellular expansion which will be relevant to the work which follows.

In view of the approximate spherical symmetry of the Wigner-Seitz cell, the crystal wave function $\psi_{\underline{k}}(\underline{r})$ can be written as a linear combination of solutions of the spherical Schrödinger equation, themselves separable into radial and angular parts, so that for a general $\underline{k}$-vector,

$$\psi_{\underline{k}}(\underline{r}) = \sum_{\ell,m} C_{\ell m} R_{\ell}(r) Y_{\ell}^{m}(\hat{\underline{r}}) \quad , \qquad (2.4.1.)$$

for a particular energy $\mathcal{E}$, where the $C_{\ell m}$ are constants to be determined from the boundary conditions on the Wigner-Seitz cell, as described below. (In practice the symmetry projection operators will be applied to this series, and many ℓ- and m-values will be eliminated). This expansion will clearly be valid in the region $r < r_i$, where r_i is the radius of the inscribed sphere of the Wigner-Seitz cell, since here the spherical harmonics form a complete set (see Figure 2.4.1., illustrating the situation for the hypothetical square lattice).



Maximum Muffin Radius for a Pure Spherical Potential

in a Square Lattice.

Figure 2.4.1.

Altmann (1974), applying the work of Saffren (1959), has shown that only in the case of a potential fully spherical out to radius r_c, the circumscribing sphere radius of the cell, is the expansion rigorously valid out to the edges of the cell. If the circumscribing sphere of one cell intersects the muffin tin spheres of neighbouring cells, then the potential within this circumscribing sphere will not be spherically symmetric in these regions of intersection; in order to avoid this intersection, the muffin tin sphere can have radius no greater than r_m, shown in Figure 2.4.1., and clearly given by

$$r_m = 2r_i - r_c \quad . \qquad (2.4.2.)$$

If the muffins intersect the circumscribing spheres, then the potential within the circumscribing sphere will contain non-spherical components. It is not, however, expected that the cellular expansion will cease to

converge immediately this rather severe condition is relaxed. Indeed, Altmann et al. (1968) have shown that the expansion converges well in the case of copper, using the Chodorow potential (see Burdick, 1963), which has a muffin radius of r_i , and Altmann et al. (1971) have also obtained good results for calcium using a potential which is non-constant all the way out to radius r_c . Results on the convergence of the cellular expansion in such a potential have not been presented in the past, so the following calculations have been made to complete the picture.

Table 2.4.1.

Convergence of Cellular Expansion for a Calcium Potential

(Band Energies Obtained)

Symmetry Point rep. \ Max^m ℓ-value	6	8	10	12
ΓA_{1g}	0.4710	0.4709	0.4710	0.4710
LE_g	0.5774	0.5752	0.5746	0.5742

It is apparent that the convergence is not as good as the muffin tin potential for copper (Altmann et al., 1968), but is still adequate, and certainly suggests that neglecting the non-spherical parts of the potential outside radius r_i , in both cases, is justified. The actual size of the correction caused by taking these regions into account will be the main subject of the calculations performed by the techniques developed in the following chapters for dealing with general non-spherical potentials.

Having established the convergence of the expansion of

equation (2.4.1.), which we now write in symmetrised form

$$\psi_k(\underline{r}) = \sum_{l,r} C_{lr} R_l(r) X_{lr}(\hat{\underline{r}}) , \qquad (2.4.3.)$$

dropping the symmetry point and representation labels from the harmonic since they remain the same throughout the rest of this section, we are now in a position to consider the boundary conditions which must be satisfied on the Wigner-Seitz cell. From the very definition of this cell it is clear that its faces are in pairs separated by a translation vector of the lattice, $\underline{T}$ say. Thus if a point $\underline{r}$ is on one face, then $\underline{r} - \underline{T}$ will be on its companion face. A simple application of Bloch's theorem tells us that, for two points on opposite faces such that

$$\underline{r}_2 = \underline{r}_1 - \underline{T} , \qquad (2.4.4.)$$

the wave functions are related by

$$\psi_k(\underline{r}_2) = \exp[i\underline{k}\cdot(\underline{r}_2 - \underline{r}_1)]\, \psi_k(\underline{r}_1) \qquad (2.4.5.)$$

and similarly for the outward normal derivatives,

$$\nabla_n \psi_k(\underline{r}_2) = \exp[i\underline{k}\cdot(\underline{r}_2 - \underline{r}_1)]\, \nabla_n \psi_k(\underline{r}_1) . \qquad (2.4.6.)$$

Inserting equation (2.4.3.) into these we obtain the boundary condition equations of the Cellular Method,

$$\sum_{l,r} C_{lr} \left\{ R_l(r) X_{lr}(\hat{\underline{r}}_2) - \exp[i\underline{k}\cdot(\underline{r}_2 - \underline{r}_1)]\, R_l(r) X_{lr}(\hat{\underline{r}}_1) \right\} = 0 , \qquad (2.4.7.)$$

$$\sum_{l,r} C_{lr} \left\{ \nabla_n [R_l(r_2) X_{lr}(\hat{\underline{r}}_2)] - \exp[i\underline{k}\cdot(\underline{r}_2 - \underline{r}_1)]\, \nabla_n [R_l(r_1) X_{lr}(\hat{\underline{r}}_1)] \right\} = 0 . \qquad (2.4.8.)$$

These are regarded as sets of equations for the constants C_{lr}, the quantities in curly brackets being evaluated at many pairs of boundary points

not related by symmetry and distributed evenly over the cell surface, as described in the account of the GEOMETRY program in Section 5.2. The expansion is curtailed at a chosen l-value, as permitted by the convergence properties, so that we have a finite set of equations.

Consider the case where n terms in the expansion are taken, and the radial and angular functions are known at p points, so that there are in total 2p (> n) boundary conditions for the n constants. These 2p equations cannot be fitted exactly, but if we write them in the form

$$\sum_{r=1}^{n} A_{sr}\, x_r = \varepsilon_s \quad , \quad s = 1, \ldots, 2p \quad , \qquad (2.4.9.)$$

where the element x_r represents the r-th C_{lr}, the element A_{sr} the value of the corresponding bracket evaluated at the s-th boundary point (the derivative boundary conditions simply being regarded as a further p points), and the ε_s are a set of residuals which should be small. The Cellular Method employs the method of least squares, minimising the sum of the squares of these residuals,

$$S^2 = \sum_{s=1}^{2p} \varepsilon_s^*\, \varepsilon_s \quad , \qquad (2.4.10.)$$

subject to the normalisation condition of the C_{lr}'s, which in the present notation becomes

$$1 = \sum_{r=1}^{n} x_r^*\, x_r \quad , \qquad (2.4.11.)$$

Substituting equation (2.4.9.) into (2.4.10.), we obtain

$$\begin{aligned} S^2 &= \sum_{s=1}^{2p} \sum_{r,u=1}^{n} x_u^*\, A_{su}^{\dagger}\, A_{sr}\, x_r \\ &= \sum_{r,u=1}^{n} x_u^*\, B_{ur}\, x_r \end{aligned} \qquad (2.4.12.)$$

where, in matrix notation,

$$\underset{\sim}{B} = \underset{\sim}{A}^{\dagger} \underset{\sim}{A} \quad , \tag{2.4.13.}$$

and the $\dagger$ denotes the conjugate of the transpose of the matrix. The minimisation of equation (2.4.12.) subject to equation (2.4.11.) is a standard Lagrangian multiplier problem, leading to the set of equations

$$\sum_{u=1}^{n} x_u^* (B_{ur} - \lambda \delta_{ur}) = 0 \quad , \tag{2.4.14.}$$

which have the familiar compatibility condition

$$\det(\underset{\sim}{B} - \lambda \underset{\sim}{I}) = 0 \quad . \tag{2.4.15.}$$

Thus the Lagrangian multiplier, λ, can be identified with the eigenvalues of the matrix $\underset{\sim}{B}$. Substituting equation (2.4.14.) into equation (2.4.12.) we can obtain the form

$$s^2 = \lambda \sum_{r=1}^{n} x_r^* x_r \tag{2.4.16.}$$

and using then equation (2.4.11.), we obtain

$$s^2 = \lambda \tag{2.4.17.}$$

It is at once apparent that the minimum value of the residual s^2 is given by the lowest eigenvalue of the matrix $\underset{\sim}{B}$, and the best set of coefficients x_r at this trial energy will be the eigenvectors of $\underset{\sim}{B}$ corresponding to the minimum λ. Now the matrix $\underset{\sim}{A}$ and hence $\underset{\sim}{B}$ and its lowest eigenvalue, λ, will depend on the trial energy, ϵ, and the successive minima of the function $\lambda(\epsilon)$ will be the energy eigenvalues of the wave function $\psi_{\underline{k}}(\underline{r})$, at the appropriate $\underline{k}$-vector, in successive bands. We shall show in Chapter 4 that the analysis following equation (2.4.10.) must be changed in the case of a non-spherical potential.

We shall now study the boundary condition matrix, $\underset{\sim}{B}$, in a little more detail. The matrix $\underset{\sim}{A}$ is in general complex, despite the fact that the symmetry adapted harmonics of O_h are real, because of the complex exponential term in equations (2.4.7.) and (2.4.8.). We write

$$\underset{\sim}{A} = \underset{\sim}{M} + i\underset{\sim}{N} \qquad (2.4.18.)$$

with elements

$$M = R_\ell(r_2) X_{\ell r}(\hat{r}_2) - \cos(\underline{k}\cdot\underline{T}) R_\ell(r_1) X_{\ell r}(\hat{r}_1) \qquad (2.4.19.)$$

and

$$N = -\sin(\underline{k}\cdot\underline{T}) R_\ell(r_1) X_{\ell r}(\hat{r}_1) \ , \qquad (2.4.20.)$$

and similar expressions for the derivative boundary conditions, where $\underline{T} = \underline{r}_2 - \underline{r}_1$. The eigenvalues of the matrix $\underset{\sim}{B}$ are required. Combining equations (2.4.13.) and (2.4.18.), we obtain

$$\underset{\sim}{B} = \underset{\sim}{P} + i\underset{\sim}{Q} \ , \qquad (2.4.21.)$$

where $\underset{\sim}{P}$ and $\underset{\sim}{Q}$ are the n × n matrices given by

$$\underset{\sim}{P} = \underset{\sim}{M}^\dagger \underset{\sim}{M} + \underset{\sim}{N}^\dagger \underset{\sim}{N} \qquad (2.4.22.)$$

and

$$\underset{\sim}{Q} = \underset{\sim}{M}^\dagger \underset{\sim}{N} - \underset{\sim}{N}^\dagger \underset{\sim}{M} \ . \qquad (2.4.23.)$$

Writing the unknown coefficients of equation (2.4.9.) also in complex form,

$$\underset{\sim}{x} = \underset{\sim}{u} + i\underset{\sim}{v} \ , \qquad (2.4.24.)$$

the eigenvalue equation

$$\underset{\sim}{B}\underset{\sim}{x} = \lambda \underset{\sim}{x} \qquad (2.4.25.)$$

is cast into the form

$$\begin{pmatrix} \underset{\sim}{P} & -\underset{\sim}{Q} \\ \underset{\sim}{Q} & \underset{\sim}{P} \end{pmatrix} \begin{pmatrix} \underset{\sim}{u} \\ \underset{\sim}{v} \end{pmatrix} = \lambda \begin{pmatrix} \underset{\sim}{u} \\ \underset{\sim}{v} \end{pmatrix} \quad , \tag{2.4.26.}$$

which is clearly a $2n \times 2n$ matrix problem. However in the case of a centro-symmetric potential, i.e. one for which

$$\bar{\bar{i}} V(\underline{r}) = V(-\underline{r}) = V(\underline{r}) \quad , \tag{2.4.27.}$$

where $\bar{\bar{i}}$ denotes the inversion operator, this can be shown to be reducible to an $n \times n$ matrix problem. Altmann (1974) has proved the following useful theorem: "If all elements of the group of the $\underline{k}$-vector $\underset{\sim}{G}^{\underline{k}}$ are either translation operators T, or operators S that (i) commute with the inversion, and (ii) are represented by real matrices, then

$$\bar{\bar{i}} \psi_{\underline{k}t} = \bar{\bar{j}} \psi_{\underline{k}t} \tag{2.4.28.}$$

for all $\underline{k}$ in the star of $\underset{\sim}{G}^{\underline{k}}$ and each column, t, of the small representation, where $\bar{\bar{j}}$ represents the conjugation operator, and $\bar{\bar{i}}$ the inversion."

The conditions of validity allow the theorem to be applied to all real small representations of symmetry for all symmorphic centro-symmetric space groups, and hence to the case in point - the group $\underset{\sim}{O}_h$. We shall apply this to the cellular expansion, when we obtain

$$\bar{\bar{i}} X_{\ell\nu}(\hat{\underline{r}}) = (-1)^{\ell} X_{\ell\nu}(\hat{\underline{r}}) \quad , \tag{2.4.29.}$$

and

$$\bar{\bar{i}} R_{\ell}(r) = R_{\ell}(r) \tag{2.4.30.}$$

due to the central symmetry of the potential, so that

$$\bar{\bar{i}} \psi_{\underline{k}}(\underline{r}) = \sum_{\ell,\nu} (-1)^{\ell} C_{\ell\nu} R_{\ell}(r) X_{\ell\nu}(\hat{\underline{r}}). \tag{2.4.31.}$$

Similarly,

$$\bar{\bar{j}}\,\psi_{\underline{k}}(\underline{r}) = \sum_{\ell,r} C^{*}_{\ell r}\, R_{\ell}(r)\, X_{\ell r}(\hat{\underline{r}}) \quad , \qquad (2.4.32.)$$

and identifying equations (2.4.31.) and (2.4.32.) through the theorem of equation (2.4.28.), we obtain

$$C^{*}_{\ell r} = (-1)^{\ell} C_{\ell r} \qquad (2.4.33.)$$

This indicates that the $C_{\ell r}$ are real and imaginary for even and odd ℓ-values respectively, so that in the above notation

$$\begin{aligned} u_{\ell r} &= 0 \quad , \quad \text{for } \ell \text{ odd} \\ v_{\ell r} &= 0 \quad , \quad \text{for } \ell \text{ even} \ , \end{aligned} \qquad (2.4.34.)$$

and the $2n \times 2n$ matrix can now be written as

$$\underset{\sim}{D} = \begin{pmatrix} \underset{\sim}{P}^{ee} & -\underset{\sim}{Q}^{eo} \\ \underset{\sim}{Q}^{oe} & \underset{\sim}{P}^{oo} \end{pmatrix} \qquad (2.4.35.)$$

and $n \times n$ matrix with

$$\begin{aligned} P^{ee}_{\ell r;\ell' r'} &= P_{\ell r;\ell' r'} \quad \ell \text{ even}, \ \ell' \text{ even} \\ Q^{eo}_{\ell r;\ell' r'} &= Q_{\ell r;\ell' r'} \quad \ell \text{ even}, \ \ell' \text{ odd} \\ Q^{oe}_{\ell r;\ell' r'} &= Q_{\ell r;\ell' r'} \quad \ell \text{ odd} \ , \ \ell' \text{ even} \\ P^{oo}_{\ell r;\ell' r'} &= P_{\ell r;\ell' r'} \quad \ell \text{ odd} \ , \ \ell' \text{ odd} \quad . \end{aligned} \qquad (2.4.36.)$$

We shall show in Chapter 4 that a similar analysis does not lead to such simplification in the non-spherical case, even though the potential remains centro-symmetric.

One further simplification occurs when $\underline{k}$ is half of a reciprocal lattice vector, for then $\exp(i\underline{k}.\underline{T})$ becomes real, so that, in the above analysis $\underset{\sim}{N}$ is a zero matrix, as consequently is $\underset{\sim}{Q}$. Thus the supermatrix form of boundary condition equation (2.4.26.) reduces to the

single n × n matrix equation

$$\underset{\sim}{P}\,\underset{\sim}{u} = \lambda\,\underset{\sim}{u} \quad , \tag{2.4.37.}$$

and the coefficients can be regarded as being real, since $\underset{\sim}{u} = \underset{\sim}{v}$. The coefficient theorem is meaningless in this case, but we still have the reduction to an n × n boundary matrix problem. This simplification occurs in the f.c.c. lattice for the symmetry points Γ , X and L. It is for this reason that we shall concentrate on energy values at these $\underline{k}$-vectors in the work which follows.

CHAPTER 3

MODIFIED POTENTIALS AND THE SCHRÖDINGER EQUATION

3.1. Introduction.

This chapter first establishes a general method of constructing the electronic potential within a crystal lattice from the individual atomic wave functions. The superposition method employed introduces non-spherical terms into the total potential within a cell, but such terms have generally been neglected in building up superposed potentials. The muffin tin approximation is then considered and it is shown that, even with this model, non-spherical components are introduced into the cellular method beyond the inscribed sphere radius if the muffin radius is larger than a certain value. This ties up with the discussion of convergence presented in Section 2.4. of the previous chapter.

Much recent discussion has been devoted to the consideration of non-spherical and non-flat potentials, the essence of which has been presented in Chapter 1. These efforts have been confined to the APW and KKR methods, and there has been some concern over how the corrections to the muffin tin potential should be introduced. It does, however, seem that the Cellular Method contains inherently such corrections, and therefore that this method should be most easily adapted to their consideration. Also, as pointed out in Chapter 1, the Cellular Method has never needed to consider a spherical boundary at any radius, since the boundary conditions are always fitted on the cell surface, so that efforts to move from potentials with spherical symmetry to those with the symmetry of the lattice should be consistent with the formulation of the method.

The necessary correction to the muffin tin potential is calculated for the f.c.c. lattice. Applications of such corrections are studied in Chapter 6 for the case of copper, where they are expected to be small.

3.2. The Formation of a Superposed Crystal Potential.

The potential about a given atom in a crystal lattice is commonly built up from atomic wave functions using the method suggested by Mattheiss (1964 a) and expanded by Loucks (1967). Loucks first obtains the atomic charge density from these wave functions and then shows how Poisson's equation may be adequately solved to give the coulomb potential about a single atom. He then builds up a superposed potential, as described below, as well as the superposed electronic charge density. The latter is used to obtain the exchange potential in the Slater approximation (or some suitable adjustment thereof), which is then added to the superposed coulomb potential to give the total crystal potential. In fact, some discussion has been devoted to the problem of whether the exchange term should be formed and then superposed, or the charge density superposed and then the total exchange potential formed; it seems that either method should give adequate results (F. Herman, private communication).

The method of superposition presented here will be essentially that expounded by Loucks, though the method will be generalised to include non-spherical terms, and the emphasis of the work changed.

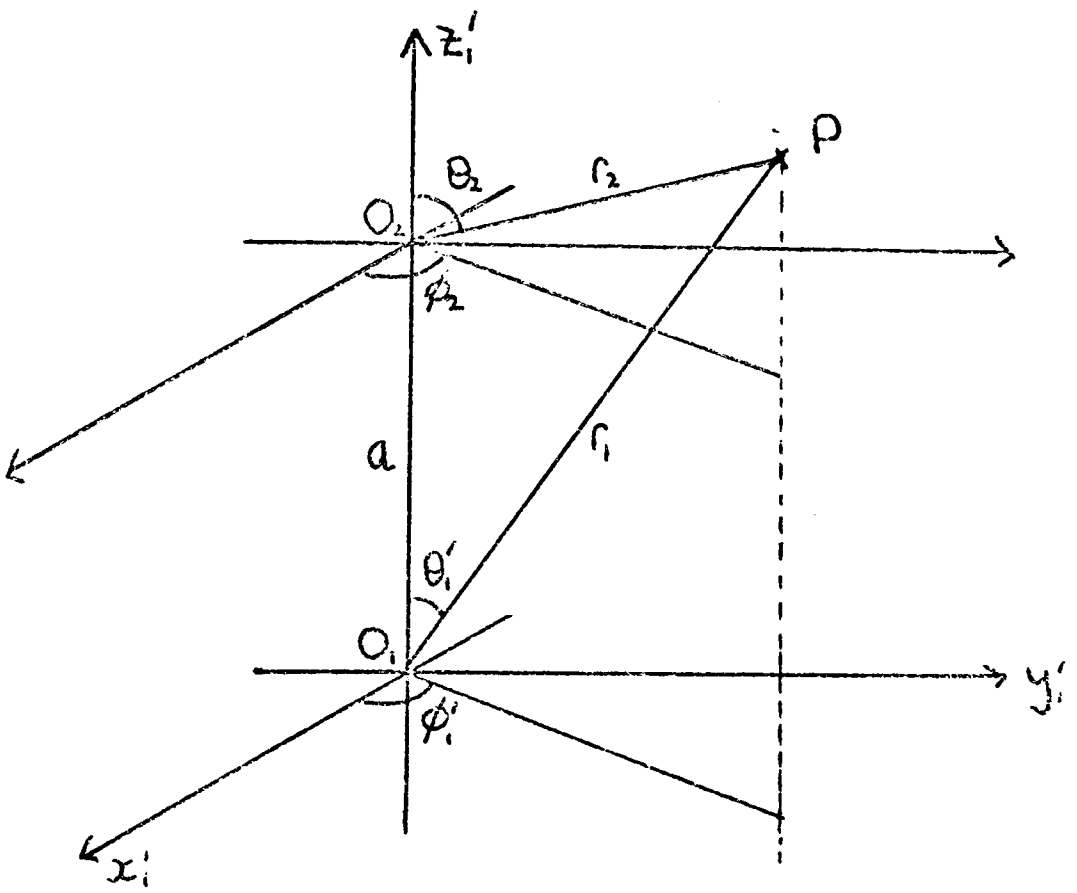


Figure 3.2.1.

Consider a function $F(r_2)$ defined at all points about the origin O_2 of Figure 3.2.1., and spherically symmetric about that origin. We require an expansion of the function in spherical harmonics about the origin O_1, a distance a from O_2. Choosing an axis z' passing through O_1 and O_2, and defining polar coordinates $r_1 \theta_1' \phi_1'$, $r_2 \theta_2 \phi_2$ as shown, it is clear from the figure that

$$r_2^2 = r_1^2 + a^2 - 2ar_1 \cos\theta_1' \qquad (3.2.1.)$$

$$r_2 \sin\theta_2 = r_1 \sin\theta_1' \quad , \qquad (3.2.2.)$$

and

$$\phi_2 = \phi_1 \qquad (3.2.3.)$$

We now expand the function $F(r_2)$ in spherical harmonics about O_1, giving

$$F(r_2) = \sum_{\ell} \alpha_\ell(r_1) Y_\ell^0(\theta_1', 0) \quad , \qquad (3.2.4.)$$

since the choice of z'-axis gives the function azimuthal symmetry, and therefore no dependence on the m-value; the expansion coefficients $\alpha_\ell(r_1)$ are given by

$$\alpha_\ell(r_1) = \int F(r_2)\, Y_\ell^{0*}(\theta_1', 0) \sin\theta_1' \, d\theta_1' \, d\phi_1' \quad , \qquad (3.2.5.)$$

where the orthonormality of the spherical harmonics has been employed. Equation (3.2.5.) reduces to

$$\alpha_\ell(r_1) = 2\pi \int_0^\pi F(r_2)\, Y_\ell^0(\theta_1', 0) \sin\theta_1' \, d\theta_1' \quad , \qquad (3.2.6.)$$

which can be integrated in steps of θ_1' using equation (3.2.1.) to obtain r_2, and hence $F(r_2)$, in terms of r_1 and θ_1'. In the case of $\ell = 0$, where

the spherical harmonic is simply $1/\sqrt{4\pi}$, equation (3.2.6.) reduces, with the help of the differential of equation (3.2.1.) at constant r_1 , to

$$\alpha_0(r_1) = \frac{\sqrt{\pi}}{a r_1} \int_{|a-r_1|}^{a+r_1} F(r_2)\, r_2\, dr_2 \quad . \tag{3.2.7.}$$

Now it may well be that the axis chosen as z' is not the z-axis of the crystal lattice as defined for the purpose of calculating symmetry adapted harmonics. We shall require an expansion of $F(r_2)$ about the real crystal axes, and must therefore use the expression

$$\begin{aligned} F(r_2) = F(a|r_1) &= \mathcal{R}_a \sum_\ell \alpha_\ell(r_1)\, Y_\ell^0(\theta_1, \phi_1) \\ &= \sum_{\ell m} \alpha_\ell(r_1)\, \mathcal{D}^\ell_{m0}(\mathcal{R}_a)\, Y_\ell^m(\theta_1, \phi_1) \quad , \end{aligned} \tag{3.2.8.}$$

where $\mathcal{R}_a$ is the rotation operator required to effect the re-orientation of the axes, θ_1 and ϕ_1 are the coordinates about new axes, and $\mathcal{D}^\ell_{m0}(\mathcal{R}_a)$ are the matrix elements of the $(2\ell + 1)$-dimensional representation of the rotation group for the rotation $\mathcal{R}_a$, as introduced in equation (2.3.2.) of the previous chapter.

Having obtained the appropriate expansion for a single neighbouring atom, we are in a position to sum over a whole set of neighbours at distance a away from O_1 , but at different orientations to the new z-axis. Considering a crystal lattice with a symmorphic space group, and point group $\underset{\sim}{G}$ containing N elements, we take a shell of n_i neighbours all at distance a_i from the central lattice site; the total contribution of this shell of neighbours to the superposed function about O_1 is obtained by summing over the point group, which includes each

neighbour at total of (N/n_i) times, so that

$$f_T(a_i|r_1) = \frac{n_i}{N} \sum_{R\in G} \sum_{l,m} \alpha_l(r_1) D^l_{mo}(R_{a_i}) R\, Y^m_l(\theta_1,\phi_1)$$

$$= \frac{n_i}{N} \sum_{l,m} \alpha_l(r_1) D^l_{mo}(R_{a_i}) \sum_{R\in G} \sum_{m'} D^l_{m'm}(R)\, Y^{m'}_l(\theta_1,\phi_1); \qquad (3.2.9.)$$

for a total of q shells, at distances a_i $(i = 1,2,\ldots,q.)$ we obtain

$$F_T(r_1) = \sum_{i=1}^{q} \frac{n_i}{N} \sum_{l,m} \alpha_l(r_1) D^l_{mo}(R_{a_i}) \sum_{R\in G} \sum_{m'} D^l_{m'm}(R)\, Y^{m'}_l(\theta_1,\phi_1) \qquad (3.2.10.)$$

i.e. an expansion in spherical harmonics which could be reduced to

$$F_T(r_1) = \sum_{l,m} \beta_{lm}(r_1)\, Y^m_l(\theta_1,\phi_1), \qquad (3.2.11.)$$

where the coefficients $\beta_{lm}(r_1)$ are given by

$$\beta_{lm}(r_1) = \sum_{i=1}^{q} \frac{n_i}{N} \sum_{m'} \alpha_l(r_1) D^l_{m'o}(R_{a_i}) \sum_{R\in G} D^l_{m'm}(R) \qquad (3.2.12.)$$

Thus the total superposed coulomb potential in the cell about which the expansion is centred will be given by

$$V_s(r_1) = V_{at}(r_1) + \sum_{l,m} \beta_{lm}(r_1)\, Y^m_l(\hat{r}_1) \qquad (3.2.13.)$$

where $V_{at}(r)$ is the atomic coulomb potential around an individual atom of the lattice; $\beta_{lm}(r)$ is given by (3.2.12.) with $\alpha_l(r)$ from (3.2.6.), where $F(r_2)$ is replaced by $V_{at}(r_2)$. Similarly the total superposed charge density in the central cell, if required, is given by

$$\rho_s(r_1) = \rho_{at}(r_1) + \sum_{l,m} \beta'_{lm}(r_1)\, Y^m_l(\hat{r}_1) \qquad (3.2.14.)$$

with similar definitions of $\rho_{at}(r)$ and $\beta'_{lm}(r)$.

These are generalised forms of the equations derived by Loucks for the spherical superposed potential, and show how even the basic superposition used in almost all band structure calculations introduces

non-spherical terms. Formulae similar to equations (3.2.10.) to (3.2.13.) will be considered in more detail in Section 3.4. of this chapter.

3.3. Muffin Tin Potentials.

It is well known that, if the cell wave functions are to be separable into radial and angular parts, any potential field used to calculate such wave functions must be spherically symmetric about the centre of the cell. As illustrated in Figure 3.3.1., for the hypothetical square lattice, this can be a genuine problem

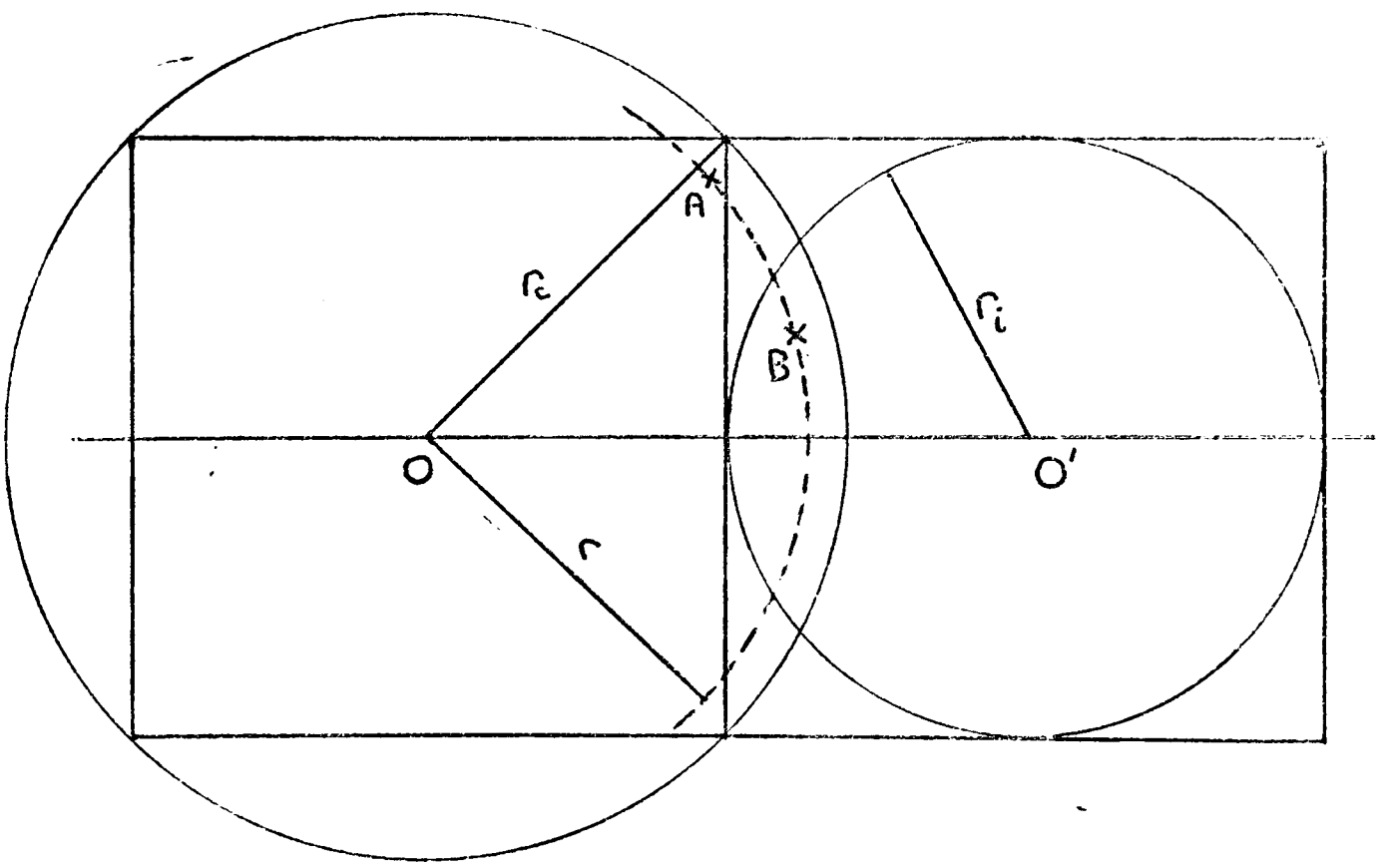


Figure 3.3.1.

if any cellular method is to be used, even if the potential about each lattice site is regarded as spherical. For, consider a sphere about the site O with radius r between r_i and r_c , as shown in the figure. The potential at a point A in the cell with centre O will be different from

that at the point B in the cell with centre at O', despite the fact that both points are at the same distance, r, from O; the potential required to calculate the wave functions in the region $r_i < r < r_c$ is, therefore not strictly spherical.

As was pointed out in Section 2.4. of the previous chapter, the cellular expansion is only strictly convergent for muffins of radius less than the quantity $(2r_i - r_c)$. This is coincident with the maximum muffin tin radius allowed if the potential is to be spherically symmetric out to r_c . This condition has been shown (see Altmann et al., 1968) to be too severe, as good band energy results have been obtained for copper with a muffin radius out to r_i , assuming the potential to be varying slowly enough between r_i and r_c to be regarded as flat outside the muffin. This suggests that any corrections introduced to take account of this non-sphericity should be very small. These corrections will be calculated as an application of the methods for dealing with non-spherical components of potential to be developed in the following chapter, and for checking these methods by showing that the corrections are indeed small. The results of such calculations will appear in Chapter 6.

It should be emphasised at this stage that the non-sphericity referred to so far in this section is inherent in the Cellular Method as it stands at present - though it has been neglected in the past - , and it is not an addition to the commonly used muffin tin potentials. Most of the methods so far used in the modified APW approach have considered a full superposed potential - as derived in Section 3.2. above - , taking a spherical average of this inside the muffin, defined as the inscribed sphere of the cell, and keeping non-spherical terms outside. Kleinman and Shurtleff (1969) criticise

this, pointing out that the potential is no longer analytic, despite the fact that much improved results have been obtained. However it would seem that physically this sort of approach ought to be appropriate in many cases, as it is the region between atomic spheres where we should expect non-spherical effects to play a part. The Cellular Method introduces non-spherical effects between the atomic spheres, but in such a way that the potential remains continuous out to the edge of the cell. The non-spherical terms are due to nearest neighbours only (cf the superposition method, where the number of neighbours considered can be varied at will), and this should be a good approximation to the truth, particularly in f.c.c. and b.c.c. lattices. It should also be noted that, as the Cellular Method solves the Schrödinger equation all the way to the cell surface, there is no need to distinguish here between "non-flat" and "non-spherical" corrections (see Chapter 1).

3.4. The Corrected Muffin Tin Potential in the Cellular Method - Application to the f.c.c. Lattice.

We return in this section to the treatment of the muffin tin potential of muffin radius r_i in the Cellular Method. The approach has been shown above to effectively neglect the variable nature of the potential in "lentils" like the shaded area shown in Figure 3.4.1. for the hypothetical square lattice. One such lentil will correspond to each nearest neighbour - twelve in the case of the f.c.c. structure (in the case of structure with a basis, i.e. more than one atom per unit cell, overlap lentils may not be restricted merely to nearest neighbours). In taking account of these lentils we shall clearly have to deal with a

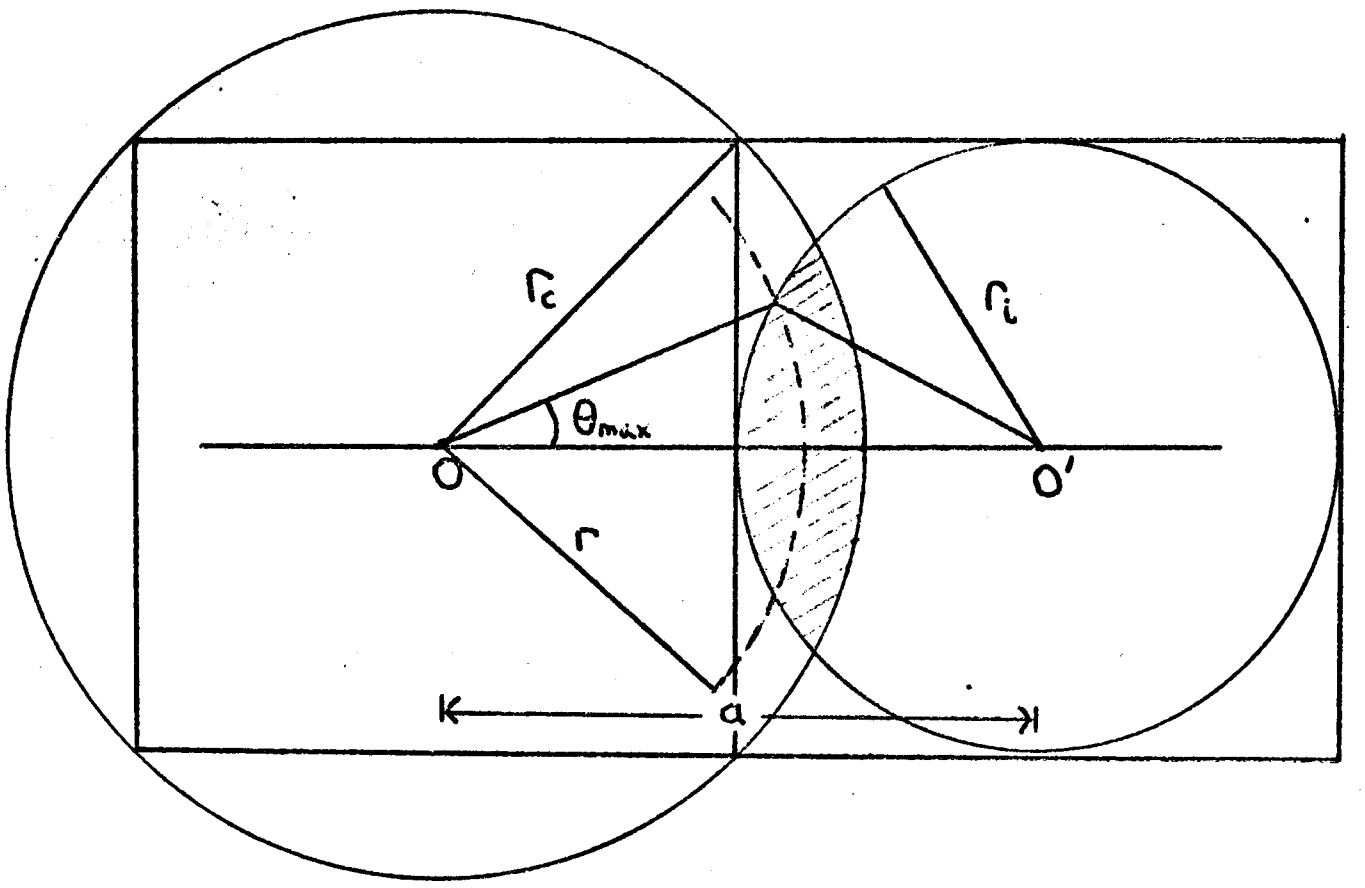


Figure 3.4.1.

non-spherical potential in the region $r_i < r < r_c$, and it will later be shown to be advantageous to aim for an expression analogous to that obtained in the general non-spherical case at the end of Section 3.2., by expanding the potential in the lentils in spherical harmonics about the central atom.

The correction which we require is the amount by which the potential in the lentils exceeds the flat value between the muffins, which we shall call V_o . The first step is, therefore, to subtract this amount from the potential within the lentils. Choosing the z-axis along the line joining the two atoms, OO' , the potential has azimuthal symmetry, so that the correction may be expanded in the form

$$V(\underline{r}) - V_o = v(\underline{r}') = \sum_l \alpha_l(r)\, Y_l^0(\hat{\underline{r}}) \qquad (3.4.1.)$$

where, using the orthonormality property of the spherical harmonics, it is clear that

$$\alpha_\ell(r) = \int_{\text{lentil}} v(\underline{r}') \, Y_\ell^{0*}(\theta,\phi) \sin\theta \, d\theta \, d\phi \quad , \qquad (3.4.2.)$$

and the integration need be taken only over the lentil since the correction potential is zero outside this. With the choice of z-axis made, we can once again write

$$r'^2 = r^2 + a^2 - 2ar\cos\theta \qquad (3.4.3.)$$

and the integral, equation (3.4.2.) becomes

$$\alpha_\ell(r) = 2\pi \int_0^{\theta_{max}} v(\underline{r}') \, Y_\ell^0(\theta,0) \sin\theta \, d\theta \quad , \qquad (3.4.4.)$$

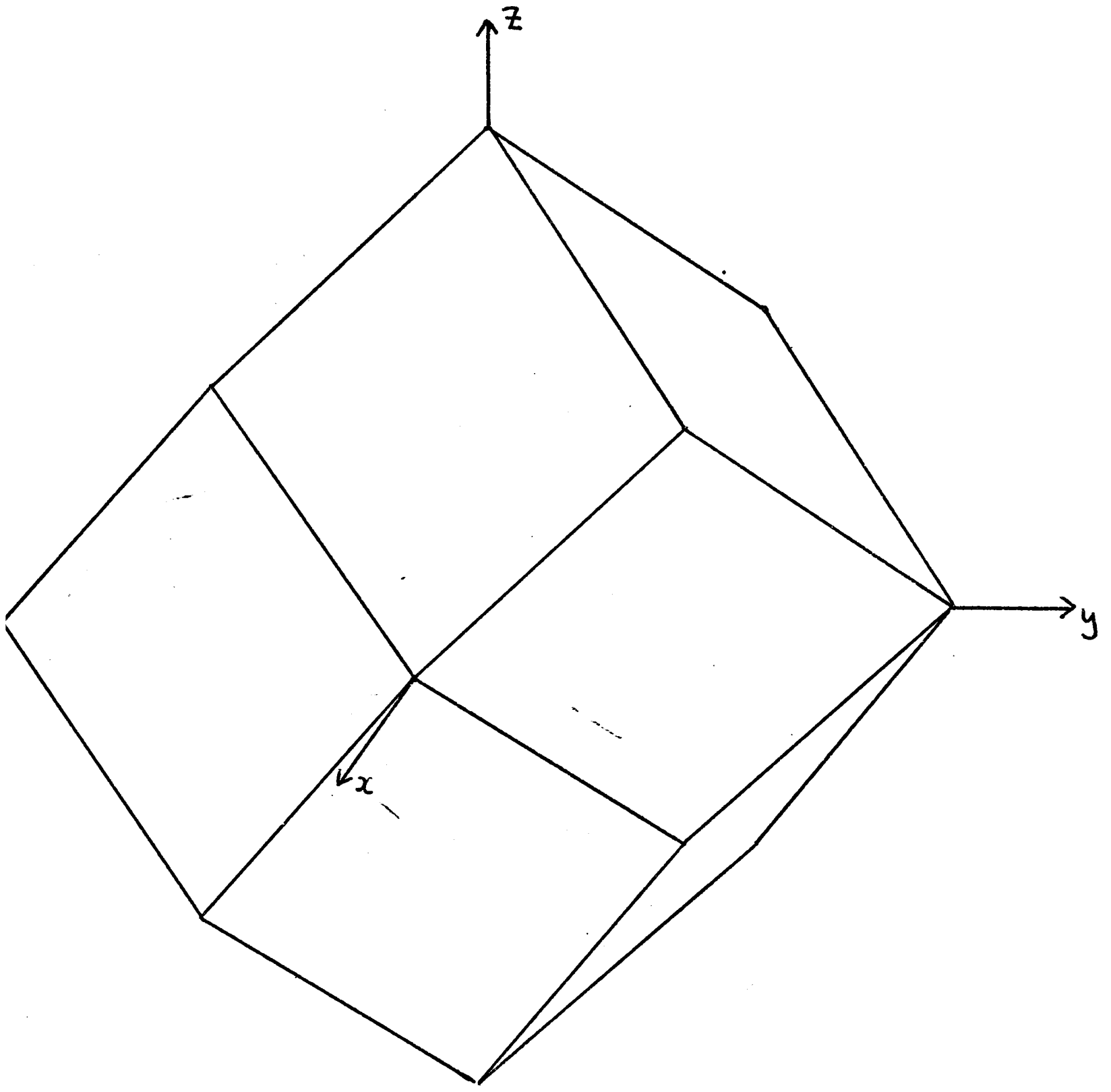
where θ_{max} is seen from Figure 3.4.1. and equation (3.4.3.) to be given by

$$\theta_{max} = \cos^{-1}\left\{\frac{r^2+a^2-r_i^2}{2ar}\right\} \qquad (3.4.5.)$$

The integral of equation (3.4.4.) is performed numerically using Simpson's rule, taking equal steps in θ along lines of constant r.

Having calculated the $\alpha_\ell(r)$ over a suitable range of r values, and up to a suitable ℓ-value, a study of the relative magnitudes of the $\alpha_\ell(r)$ with increasing ℓ-value will reveal the best ℓ-value at which to truncate the series of equation (3.4.1.). We must bear in mind, however, that several ℓ-values will disappear, due to the symmetry of the lattice, when the sum over all lentils of overlap is taken.

We shall now consider the complete set of overlaps around the Wigner-Seitz cell of the structure being considered. The cell may have all faces the same (as in the f.c.c. lattice, where the unit cell is as shown in Figure 3.4.2.) or two or more differently shaped faces (as in the b.c.c. lattice, the cell being a truncated octohedron with eight hexagonal and four square faces). By making use of the symmetry group



Wigner-Seitz Cell of the f.c.c. Lattice.

Figure 3.4.2.

operations of the lattice, as in Section 3.2., it proves necessary to calculate the $\alpha_\ell(r)$ only once for each type of face. In a manner also analogous to Section 3.2., the expansion of equation (3.4.1.) is reorientated along the crystal axes, and then summed over all neighbours in the shell concerned. For the f.c.c. lattice it is clear from Figure 3.4.2. that the rotation operator

$$S = S(0, \pi/4, 0), \qquad (3.4.6.)$$

in terms of the usual Euler angles, will effect the required reorientation, casting equation (3.4.1.) into the form

$$v'(\underline{r}) = \sum_{\ell,m} \alpha_\ell(r)\, \mathcal{D}^\ell_{m0}(S)\, Y^m_\ell(\hat{\underline{r}}) \qquad (3.4.7.)$$

Next we note that the 48 operations of the point group of the f.c.c. lattice, O_h , will rotate each of the twelve faces of the unit cell into the first (for which the correction has just been calculated) four times. Thus the total correction potential is given by

$$V'_T(\underline{r}) = \frac{1}{4} \sum_{R \in O_h} \mathcal{R}\, v'(\underline{r}) \qquad (3.4.8.)$$

which, substituting for $v'(\underline{r})$ from equation (3.4.7.) and using again the properties of the spherical harmonics as bases of the representations of the rotation group, we obtain

$$V'_T(\underline{r}) = \frac{1}{4} \sum_{R \in O_h} \sum_{\ell,m} \alpha_\ell(r)\, \mathcal{D}^\ell_{m0}(S) \sum_{m'} \mathcal{D}_{m'm}(R)\, Y^{m'}_\ell(\hat{\underline{r}}) , \qquad (3.4.9.)$$

which may be written in the form

$$V'_T(\underline{r}) = \sum_\ell \alpha_\ell(r) \sum_m f(\ell, m)\, Y^m_\ell(\hat{\underline{r}}) \qquad (3.4.10.)$$

where

$$f(\ell, m) = \frac{1}{4} \sum_{R \in O_h} \sum_{m'} \mathcal{D}^\ell_{m'm}(R)\, \mathcal{D}^\ell_{m0}(S) \qquad (3.4.11.)$$

As would be expected, the $f(\ell,m)$ turn out to be related to the coefficients of the spherical harmonics appearing in the symmetry adapted harmonics of the totally symmetric representation of $\underset{\sim}{O}_h$, ΓA_{1g} (see previous chapter), so that equation (3.4.10.) could be written

$$V'_T(\underline{r}) = \sum_{\ell,r} \alpha'_{\ell r}(r)\, X^{\Gamma A_{1g}}_{\ell r}(\hat{\underline{r}}) \,, \qquad (3.4.12.)$$

where the $X^{\Gamma A_{1g}}_{\ell r}(\hat{\underline{r}})$ are the harmonics of ΓA_{1g}, and the $\alpha'_\ell(r)$ a revised set of expansion coefficients. This form will be explored again in Chapter 4. For the present, a derivation of the $f(\ell,m.)$ will serve to produce a form which is directly computable, and to establish the properties of the expansion (3.4.10.).

From equations (2.3.3.) and (2.3.4.) of the previous chapter, it is clear that, when S is given by equation (3.4.6.),

$$\mathcal{D}^\ell_{mo}(S) = d^\ell_{mo}(\pi/4) \,. \qquad (3.4.13.)$$

Now the sum over the group $\underset{\sim}{O}_h$ of equation (3.4.11.) can be performed with the aid of Table 2.3.1. of the previous chapter, and gives us

$$\sum_{R\in\underset{\sim}{O}_h} \mathcal{D}^\ell_{m'm}(R) = \begin{cases} 8\left[\delta_{m',m} + \delta_{m',-m} + 4\, d^\ell_{m'm}(\pi/2)\right] & \text{for } \begin{cases} \ell = 0,4,6,8,\ldots \\ |m|, |m'| = 0,4,8,\ldots \end{cases} \\ 0 \,, \text{ otherwise} \end{cases} \qquad (3.4.14.)$$

Using the results of equations (3.4.13.) and (3.4.14.) in equation (3.4.11.) we obtain

$$\begin{aligned} F(\ell,m) &= 2\sum_{m'} d^\ell_{m'o}(\pi/4)\left[\delta_{m',m} + \delta_{m',-m} + 4\, d^\ell_{m'm}(\pi/2)\right] \\ &= 2\left[2\, d^\ell_{mo}(\pi/4) + 4\sum_{m'} d^\ell_{m'o}(\pi/4)\, d^\ell_{m'm}(\pi/2)\right] \\ &= 4\left[d^\ell_{mo}(\pi/4) + 2 d^\ell_{oo}(\pi/4)\, d^\ell_{mo}(\pi/2) + 4\sum_{m'>0} d^\ell_{m'o}(\pi/4)\, d^\ell_{m'm}(\pi/2)\right] \end{aligned} \qquad (3.4.15.)$$

where the sum over m' takes $m' = 4,8,12,\ldots \leq \ell'$, and we have used the identity, easily shown from equation (3.4.17.) below,

$$d^{\ell}_{m0}(\beta) = (-1)^{m} d^{\ell}_{-m0}(\beta) \quad . \qquad (3.4.16.)$$

The Table 3.4.1. below gives the non-zero values of $f(\ell, |m|)$ up to $\ell = 12$ - it is clear from the properties of the $d^{\ell}_{m'm}(\beta)$ that $f(\ell,m)$ will depend only on $|m|$. In order to calculate the $d^{\ell}_{nm}(\pi/4)$ we have used the standard formula (see, for example, Tinkham, 1964)

$$d^{\ell}_{nm}(\beta) = \sum_{k} \frac{(-1)^{k-n+m}\sqrt{(\ell+n)!\,(\ell-n)!\,(\ell+m)!\,(\ell-m)!}}{(\ell-n-k)!\,(\ell+m-k)!\,(k-m+n)!\;k!} \cos^{2\ell+m-n-2k}(\beta/2)\cdot\sin^{2k-m+n}(\beta/2) \,. \qquad (3.4.17.)$$

Table (3.4.1.)

Numerical Coefficients in the Non-spherical Potential Expansion.

ℓ	m	$f(\ell, m)$
0	0	12
2	0	0
4	0	-1.7500
4	4	-1.0458
6	0	-2.4375
6	4	4.5601
8	0	3.4805
8	4	1.3088
8	8	1.9942
10	0	-6.3477×10^{-2}
10	4	6.3954×10^{-2}
10	8	7.6136×10^{-2}
12	0	-1.0714
12	4	-3.1225
12	8	3.6308
12	12	-1.5557

It is interesting to note that the $\ell = 10$ harmonics will contribute little to the expansion of equation (3.4.10.), owing to their very low $f(\ell,m)$ coefficients, apparent from Table (3.4.1.). This fact will prove very useful in enabling us to truncate the expansion for the correction potential at $\ell = 8$ in the work which follows.

3.5. The New Form of the Schrödinger Equation.

The Schrödinger equation can be written, as in the previous chapter, in the form

$$\nabla^2 \phi(\underline{r}) + 2\left[\tfrac{1}{2}\epsilon + V(\underline{r})\right]\phi(\underline{r}) = 0 , \qquad (3.5.1.)$$

with $V(\underline{r})$ in negative atomic units and ϵ in Rydbergs. Now the potential, $V(\underline{r})$, in the case under consideration is given by the sum of the original muffin tin potential, $V(r)$, together with the correction potential, $V_T'(\underline{r})$ from the previous section, so that

$$V(\underline{r}) = V(r) + \sum_{\ell} \alpha_\ell(r) \sum_{m} F(\ell,m)\, Y_\ell^m(\hat{\underline{r}}) . \qquad (3.5.2.)$$

In the case of a spherical potential it has been shown that the wave function is separable into radial and angular parts, as

$$\phi_{\ell m}(\underline{r}) = R_\ell(r)\, Y_\ell^m(\hat{\underline{r}}) \qquad (3.5.3.)$$

(see Chapter 2, equation (2.2.3.)). However, the potential of equation (3.5.2.) is not spherical, and the wave function will no longer be separable into radial and angular parts. We must write the wave function in the more general form

$$\phi(\underline{r}) = \sum_{\ell,m} R_\ell^m(r)\, Y_\ell^m(\hat{\underline{r}}) , \qquad (3.5.4.)$$

which is equivalent to the above expansion of the potential in spherical harmonics, and is the form employed by Evans and Keller (1971) as described in Chapter 1 above. Note that the new radial functions have become dependent on the azimuthal quantum number, m . Inserting this proposed solution into the Schrödinger equation (3.5.1.) along with the potential of equation (3.5.2.), we obtain

$$\sum_{\ell,m}\left\{\nabla^2+2\left[\tfrac{1}{2}\epsilon+V(r)+\sum_{\ell''}\alpha_{\ell''}(r)\sum_{m''}F(\ell'',m'')\,Y_{\ell''}^{m''}(\hat{\underline{r}})\right]\right\}R_\ell^m(r)\,Y_\ell^m(\hat{\underline{r}})=0. \qquad (3.5.5.)$$

Now multiplying equation (3.5.5.) through by $Y_{\ell'}^{m'*}(\hat{\underline{r}})$ and integrating over angular coordinates, we obtain

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR_{\ell'}^{m'}(r)}{dr}\right]-\left[\frac{\ell'(\ell'+1)}{r^2}-\epsilon-2V(r)\right]R_{\ell'}^{m'}(r)$$

$$+2\sum_{\ell,m}\sum_{\ell'',m''}\alpha_{\ell''}(r)\,F(\ell'',m'')\,G(\ell',m';\ell'',m'';\ell,m)\,R_\ell^m(r)=0, \qquad (3.5.6.)$$

where

$$G(\ell',m';\ell'',m'';\ell,m)=\int Y_{\ell'}^{m'*}(\hat{\underline{r}})\,Y_{\ell''}^{m''}(\hat{\underline{r}})\,Y_\ell^m(\hat{\underline{r}})\,d\Omega \qquad (3.5.7.)$$

are the Gaunt numbers, as defined, for example, by Rotenberg et al. (1959). Writing

$$a_{\ell\ell'}^{mm'}(r)=\sum_{\ell'',m''}\alpha_{\ell''}(r)\,F(\ell'',m'')\,G(\ell,m;\ell'',m'';\ell',m') \qquad (3.5.8.)$$

the radial equation becomes

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR_\ell^m(r)}{dr}\right]-\left[\frac{\ell(\ell+1)}{r^2}-\epsilon-2V(r)\right]R_\ell^m(r)+2\sum_{\ell',m'}a_{\ell\ell'}^{mm'}(r)\,R_{\ell'}^{m'}(r)=0. \qquad (3.5.9.)$$

The m-dependence of the radial functions clearly arises from the coefficients $a_{\ell\ell'}^{mm'}(r)$, which are also responsible for coupling the equations for the radial functions - since it now appears that, in principle each radial function depends on all others, through the final term of equation

(3.5.9.). The general solution of this resulting set of coupled equations is the concern of the following chapter, but here we shall proceed to consider in detail the properties of the coupling coefficients $a_{\ell\ell'}^{mm'}(r)$ in the case of the muffin tin potential in the f.c.c. lattice, in the hope that the number of equations coupling together can be reduced appreciably by the symmetry properties of the lattice - taking equation (3.5.9.) as it stands, there are in principle, for a cellular expansion up to $\ell = 12$, 169 coupled equations in the set! Sections 3.6. and 3.7. will prove useful also in the context of the work of Kleinman and Shurtleff presented in Section 1.3. above enabling their ideas to be executed without recourse to the modified APW form which they employ.

3.6. Useful Properties of the Coupling Coefficients.

In the case under consideration, the coupling coefficients, as defined in equation (3.5.8.), are non-zero only in the region between r_i and r_c, as they are derived from the correction potential developed in Section 3.4. We shall take the properties of the $f(\ell,m)$ defined in that section together with well known properties of the Gaunt numbers (see Rotenberg et al., 1959) in order to deduce properties of the coupling coefficients. This work will serve as an example for similar calculations on different lattices, where the $f(\ell,m)$ will be different.

The following properties of the Gaunt numbers will be required:

$$G(\ell,m;\ell'',m'';\ell',m') = G(\ell,-m;\ell'',-m'';\ell',-m') \quad , \qquad (3.6.1.)$$

$$G = 0 \quad \text{unless} \quad \ell + \ell' + \ell'' \text{ is even,} \qquad (3.6.2.)$$

$$G = 0 \quad \text{unless} \quad m = m' + m'' \quad , \tag{3.6.3.}$$

and

$$G(\ell,m;\ell'',m'';\ell',m') = G(\ell',m';\ell'',m'';\ell,m) \ . \tag{3.6.4.}$$

We also quote the following properties of the $f(\ell,m)$, apparent from equations (3.4.13.) to (3.4.15.) and the properties of the $d_{nm}(\pi/2)$ expounded in the previous chapter:

$$f(\ell,m) = f(\ell,-m) \quad , \tag{3.6.5.}$$

$$f(\ell,m) = 0 \quad \text{unless} \quad \ell = 0,4,6,8,\ldots \quad |m| = 0,4,8,\ldots \tag{3.6.6.}$$

Now, applying the properties (3.6.1.) and (3.6.5.) to the expression for the coupling coefficients, equation (3.5.8.) may be rewritten

$$a^{mm'}_{\ell\ell'}(r) = \sum_{\ell''} \alpha_{\ell''}(r) \Big\{ F(\ell'',0)\, G(\ell,m;\ell'',0;\ell',m') + \sum_{m''>0} F(\ell'',m'')\big[G(\ell,m;\ell'',m'';\ell',m') + G(\ell,-m;\ell'',m'';\ell',-m')\big] \Big\} \ . \tag{3.6.7.}$$

In this form it is easily seen that

$$a^{mm'}_{\ell\ell'}(r) = a^{-m-m'}_{\ell\ell'}(r) \tag{3.6.8.}$$

and

$$a^{mm'}_{\ell\ell'}(r) = a^{m'm}_{\ell'\ell}(r) \ . \tag{3.6.9.}$$

Equations (3.6.2.) and (3.6.6.) together imply that

$$a^{mm'}_{\ell\ell'}(r) = 0 \quad \text{unless} \quad \ell,\ell' \text{ are both even or both odd,} \tag{3.6.10.}$$

whilst equations (3.6.3.) and (3.6.6.) together imply

$$a^{mm'}_{\ell\ell'}(r) = 0 \quad \text{unless} \quad m,m' \text{ are both even or both odd.} \tag{3.6.11.}$$

Indeed this latter property can be taken a stage further, since we see from equation (3.6.6.), that the f(ℓ,m) are only non-zero when m is a multiple of 4, or zero, so that the m and m' of equation (3.6.11.) must in fact differ by zero or a multiple of 4.

Equation (3.6.8.) can also be taken a stage further to provide a useful property of the radial functions $R_\ell^m(r)$. Replacing m by -m in equation (3.5.9.) gives

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR_\ell^{-m}(r)}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right]R_\ell^{-m}(r) + 2\sum_{\ell',m'} a_{\ell\ell'}^{-mm'}(r)\,R_{\ell'}^{m'}(r) = 0. \quad (3.6.12.)$$

Since the summation of equation (3.6.12.) is over all possible m'($|m'| \leq \ell'$), we may change the sign of both m 's within the summation; then applying equation (3.6.8.), we obtain

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR_\ell^{-m}(r)}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right]R_\ell^{-m}(r) + 2\sum_{\ell',m'} a_{\ell\ell'}^{mm'}(r)\,R_{\ell'}^{-m'}(r) = 0, \quad (3.6.13.)$$

whilst at some radius, r_o , where the non-spherical potential first becomes non-zero, we have the initial condition

$$R_\ell^m(r_o) = R_\ell(r_o) \quad , \quad \forall\ m \qquad (3.6.14.)$$

Therefore, given these starting values, the $R_\ell^{-m}(r)$ satisfy the same equation as the $R_\ell^m(r)$ and are consequently identical. This immediately cuts by nearly half the number of coupled equations in the set of equation (3.5.9.) requiring solution.

The properties (3.6.10.) and (3.6.11.) imply four broad categories of coupling coefficients.

(a) even ℓ-values, even m-values,
(b) even ℓ-values, odd m-values,
(c) Odd ℓ-values, even m-values,
(d) odd ℓ-values, odd m-values,

so that, for instance $R_{\ell}^{m}(r)$ with ℓ even and m odd will only couple to others with ℓ even and m' odd, and only the category (b) coupling coefficients will be required. Further only half of this category will be required since the m and m' must differ by zero or a multiple of 4 (i.e. must be the same when written modulo-4) as deduced above, thus effectively further dividing each category into two sub-categories. Assuming, for the moment, the categories to be approximately the same size we have therefore effectively reduced by a factor approaching 16 the total number of equations which are coupled together. This is very important in that large amounts of computing time and space can be saved if these properties are used to the full. However, programming details will concern us in Chapter 5 and we shall postpone further discussion on this subject until then.

In this section we have developed a set of useful properties of the coupling coefficients in order to minimise the problem of solution of the equations for the radial functions to be discussed in the following chapter. These are the only simplifications possible in the general case. We shall now proceed, in the following section, to discuss the further simplifications which can be used when calculating energy levels at points of symmetry in k-space.

3.7. The Radial Equation for Points of Symmetry in k-space.

The form of solution of the Schrödinger equation in the non-spherical case, equation (3.5.4.) is in effect nothing more than an expansion of the wave function, $\phi(\underline{r})$ in terms of the complete set of spherical harmonics, just as the non-spherical potential was expanded in similar form in Section 3.2. above. When dealing with a symmetry point in k-space it proves useful to expand the wave function in the complete

set of symmetry adapted harmonics of the appropriate $\underline{k}$-vector (see discussion at the end of Section 2.3. of the previous chapter). Then equation (3.5.4.) is replaced by

$$\phi_k(\underline{r}) = \sum_{j,L} R_L^{kj}(r)\, X_L^{kj}(\hat{\underline{r}}) \quad , \qquad (3.7.1.)$$

and from the properties of the symmetry projection operators, W_{ts}^{ki}, discussed in Section 2.3., it is clear that for a function symmetry adapted to the i-th representation of the group $\underset{\sim}{G}^k$, all terms in the summation over j, except $j = i$, will vanish. Similarly, the potential, given in equation (3.5.2.) will be expanded in the symmetry adapted harmonics of the totally symmetric representation of the crystal symmetry group, denoted by ΓA_{1g}, i.e.

$$V(\underline{r}) = V(r) + \sum_{L''} \alpha_{L''}(r)\, X_{L''}^{\Gamma A_{1g}}(\hat{\underline{r}}) \quad , \qquad (3.7.2.)$$

where L'' is the usual double suffix, representing ℓ-value and partner index, ν. Substituting equations (3.7.1.) and (3.7.2.) into the Schrödinger equation (3.5.1.), multiplying through by $X_L^{kj}(\hat{\underline{r}})$, and integrating over all solid angle, we obtain the radial equation analogous to equation (3.5.6.)

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2 \frac{dR_L^{kj}(r)}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right] R_L^{kj}(r)$$

$$+ 2 \sum_{j',L',L''} \alpha_{L''}(r) \int X_L^{kj}(\hat{\underline{r}})\, X_{L''}^{\Gamma A_{1g}}(\hat{\underline{r}})\, X_{L'}^{kj'}(\hat{\underline{r}})\, d\Omega \,.\, R_{L'}^{kj'}(r) = 0 \,. \qquad (3.7.3.)$$

Before defining the new coupling coefficients arising from the final term of the equation, it is worth studying the properties of the angular integration in this term. We shall show that a considerable simplification can be effected if the integral is regarded as the overlap integral of a basis function of the direct product of the representations j and j', $\left[X_L^{kj}(\hat{\underline{r}})\, X_{L'}^{kj'}(\hat{\underline{r}})\right]$ with a basis function of the representation ΓA_{1g}, $\left[X_L^{\Gamma A_{1g}}(\hat{\underline{r}})\right]$.

This direct product representation is in general reducible. We shall show below that the direct product representation contains the representation ΓA_{1g} only along the diagonal, $j = j'$, so that the overlap integral of their basis functions with those of ΓA_{1g} must vanish except when $j = j'$. Williams and Morgan (1974) use this fact in their work, but without proof; we shall now present a formal proof of the observation. The necessary group theoretical results can be found, for example, in Tinkham (1964).

A well known group theoretical theorem states that the frequency of occurrence of the irreducible representation ${}^{j}D$ in the reducible representation, H , of the same group, $\underset{\sim}{G}$ of operators $\mathcal{R}$, is given by

$$f({}^{j}D|H) = |\underset{\sim}{G}|^{-1} \sum_{\mathcal{R}\in\underset{\sim}{G}} \chi^{j}(\mathcal{R})^{*} \chi(\mathcal{R}) \quad , \qquad (3.7.4.)$$

where $\chi^{j}(\mathcal{R})$ is the character of $\mathcal{R}$ in the irreducible representation ${}^{j}D$, and $\chi(\mathcal{R})$ that of the reducible representation H , whilst $|\underset{\sim}{G}|$ denotes the order of the group $\underset{\sim}{G}$. It is also well known that for a direct product of the irreducible representations ${}^{i}D$ and ${}^{j}D$,

$$\chi(\mathcal{R}) = \chi^{i}(\mathcal{R}) . \chi^{j}(\mathcal{R}) \quad , \qquad (3.7.5.)$$

and that the characters of the totally symmetric representation,

$$\chi^{1}(\mathcal{R}) = 1 \quad , \qquad \forall\, \mathcal{R} \in \underset{\sim}{G} \qquad (3.7.6.)$$

Writing

$$H = {}^{i}D \times {}^{j}D \qquad (3.7.7.)$$

we obtain from the theorem of equation (3.7.4.), using the results of equations (3.7.5.) and (3.7.6.),

$$f(^1D\,|\,^iD\times{}^jD) = |G|^{-1}\sum_R \chi^i(R)\chi^j(R)\,. \qquad (3.7.8.)$$

Now, if all the characters are real, as is the case for the group O_h ; the orthogonality of characters tells us that

$$\sum_{R\in G} \chi^i(R)\,\chi^j(R) = |G|\,\delta_{ij}\quad , \qquad (3.7.9.)$$

and inserting this into equation (3.7.8.), we obtain immediately the required result:

$$f\,(^1D\,|\,^iD\times{}^jD) = \delta_{ij}\,. \qquad (3.7.10.)$$

We shall now proceed to apply this result to the angular integral of equation (3.7.3.) to give the result

$$\int X_L^{kj}(\hat{r})\,X_{L''}^{\Gamma A_{ig}}(\hat{r})\,X_{L'}^{kj'}(\hat{r})\,d\Omega = 0\quad , \quad j\neq j'\ , \qquad (3.7.11.)$$

so that we define the symmetrised coupling coefficients in the form

$$a_{LL'}^j(r) = \sum_{L''}\alpha_{L''}(r)\int X_L^{kj}(\hat{r})\,X_{L''}^{\Gamma A_{ig}}(\hat{r})\,X_{L'}^{kj}(\hat{r})\,d\Omega\quad , \qquad (3.7.12.)$$

and the radial equation becomes

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR_L^j(r)}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right]R_L^j(r) + 2\sum_{L'}a_{LL'}^j(r)R_{L'}^j(r) = 0 \qquad (3.7.13.)$$

where we now understand the j superscript to indicate also the appropriate k-vector. It is at once apparent that the amount of coupling has been considerably reduced by the properties of this Gaunt-type integral, since now the radial functions, $R_L^j(r)$, only couple to the radial functions of the same representation of the group, not to those of the whole group. This can represent, particularly in the case of points of high symmetry in k-space,

a large reduction in the amount of work required to solve the band energy problem. It now remains to be shown how these symmetrised coupling coefficients might be obtained most easily from the $a_{\ell\ell'}^{mm'}(r)$ of above.

The symmetry adapted harmonics were defined in Chapter 2, and given as linear combinations of the spherical harmonics by the equation (2.3.6.), repeated here for convenience:

$$X_L^{kj}(\hat{\underline{r}}) = \sum_m A_{Lm}^{kj} \; Y_\ell^m(\hat{\underline{r}}) \qquad (3.7.14.)$$

Using this definition in equation (3.7.12.), together with the definition of the $a_{\ell\ell'}^{mm'}(r)$ from equation (3.5.8.), and once again compressing the $\underline{k}, j$ notation into the j , we obtain

$$a_{LL'}^{j}(r) = \sum_{m,m'} A_{Lm}^{j} \; A_{L'm'}^{j} \, a_{\ell\ell'}^{mm'}(r) \quad , \qquad (3.7.15.)$$

and the properties of the $a_{\ell\ell'}^{mm'}(r)$ derived in the previous section can be used to simplify the calculations from this equation. The manipulation of this expression is dealt with in Section 5.5. below.

3.8. Summary.

This chapter has performed a series of functions which it will be useful to summarise before progressing to the actual solution of the non-spherical problem in general. Firstly we have shown how the method of superposition developed by Mattheiss (1964 a), and often used for the calculation of crystal potentials, leads to a non-spherical crystal potential, and obtained the exact expression for this potential in the case of an f.c.c. lattice. Secondly we study the muffin tin approximation as used in the Cellular Method, show that we are in fact neglecting non-spherical

contributions to the potential in the outer regions of the cell, and calculate an expression for these corrections again for an f.c.c. lattice. The methods developed in the following chapter will be applied to this correction and the results are presented in the final chapter.

The two ways in which non-spherical potentials are shown to arise both lead to identical expansions for the non-spherical parts. We then show how this general form of correction affects the Schrödinger equation, and finally show how the symmetry properties first of the lattice and then of the k-vector being considered may be used to simplify the equation derived for the new radial functions. These properties will be applied in the following chapter, where we consider the general solution of the non-spherical problem.

CHAPTER 4

THE CELLULAR METHOD FOR NON-SPHERICAL POTENTIALS

4.1. Introduction.

In Section 3.5. of the previous chapter we showed that the introduction of a non-spherical potential into the Schrödinger equation leads to solutions of a very different character from those derived for the spherical case in Chapter 2. Our principal tasks in this chapter will be the solution of the new radial equation derived in the previous chapter, and the use of these new solutions in the Cellular Method.

We first indicate how the new form of solution can be written as a generalisation of the spherical solutions by introducing a second pair of angular momentum quantum numbers, and the significance of these quantum numbers is illustrated. The correct form of the cellular expansion in the case of a non-spherical potential is at once clear.

Secondly we show that this form of the cellular expansion is necessary to the solution of the coupled equations developed in Section 3.5. Since this set of coupled equations result in radial functions depending on one another, the relative sizes of these functions, appearing in the coupling term, are important, and therefore special care must be taken over the normalisation of these functions. This approach, as well as confirming the new form of the cellular expansion also suggests a further, iterative, method of solving the band problem. This method is fully investigated, since, as will become apparent, the method first developed is rather expensive in computing time, although formally equivalent to the usual Cellular Method, and relatively simple to apply.

The actual solution of the radial equations obtained is then considered, two numerical techniques being suggested. The general problem is shown to be very large, and the application of the symmetry properties of the lattice to simplify the coupled equations is considered.

The new form of the cellular expansion, although similar in principle to that of the spherical case, requires some careful consideration when we proceed to use this as a trial function in the Cellular Method. Certain modifications to the boundary condition fitting are required, and some of the theorems developed in conjunction with the method (see Section 2.4. above) require modification. These problems will be considered in Section 4.5.

In view of the large number of radial functions which must be calculated in the full treatment developed in this chapter, the search for a suitable quicker approximate technique is of importance. The iterative approximation suggested above, and described fully in Section 4.6., will prove to be the best of those investigated, but it is worth recording an earlier attempt at the problem. It is often the case, when treating a problem variationally, that the trial wave function used is not a solution of the Schrödinger equation for the problem. Convenient trial functions of this type were tried here, and the method is described in the Appendix to this chapter, whilst the results appear, along with those for the other methods, in Chapter 6.

Throughout this chapter we shall use the following notational convenience - the composite suffix L will represent the angular momentum quantum numbers ℓ,m (or in the symmetry adapted case the ℓ-value and partner index, ν).

4.2. A Consideration of the New Radial Equation.

We showed in the previous chapter how, for a potential written in the form

$$V(\underline{r}) = V(r) + \sum_{L''} \alpha_{L''}(r)\, Y_{L''}(\hat{\underline{r}}) \,, \qquad (4.2.1.)$$

the solutions of the Schrödinger equation, no longer separable into radial and angular parts, are of the form

$$\phi(\underline{r}) = \sum_{L} R_L(r)\, Y_L(\hat{\underline{r}}) \ , \qquad (4.2.2.)$$

where the radial functions, $R_L(r)$ satisfy the equation

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2 \frac{dR_L(r)}{dr}\right] - \left[\frac{l(l+1)}{r^2} - \epsilon - 2V(r)\right]R_L(r) + 2\sum_{L'} a_{LL'}(r) R_{L'}(r) = 0, \qquad (4.2.3.)$$

and

$$a_{LL'}(r) = \sum_{L''} \alpha_{L''}(r) \int Y_L^*(\hat{\underline{r}})\, Y_{L''}(\hat{\underline{r}})\, Y_{L'}(\hat{\underline{r}})\, d\Omega \ . \qquad (4.2.4.)$$

The equation (4.2.3.) defines the new radial functions, which are now dependent on the azimuthal quantum number, m, as well as depending on one another through the coupling term. The equation is analogous to that obtained in the work of Evans and Keller (1971) described in Chapter 1. of this thesis.

In the case of a spherical potential, the solutions corresponding to that of equation (4.2.2.), were a set of functions of the form

$$\phi_L(\underline{r}) = R_l(r)\, Y_L(\hat{\underline{r}}) \ . \qquad (4.2.5.)$$

This suggests that there ought to be more than one possible solution of the form of equation (4.2.2.), as the introduction of a small non-spherical part to the potential should not alter the number of possible solutions. We therefore suggest the form

$$\phi_L(\underline{r}) = \sum_{L'} \mathcal{R}_{L'L}(r)\, Y_{L'}(\hat{\underline{r}}) \ , \qquad (4.2.6.)$$

where the radial functions are now labelled by two sets of quantum numbers,

and such that in a region of spherical potential

$$\mathcal{R}_{L'L}(r) = R_\ell(r)\,\delta_{L',L} \qquad (4.2.7.)$$

The form of equation (4.2.6.) is not new, and was introduced by John et al. (1972), as described in Chapter 1 above. The justification of this expression will become apparent below, and further discussion will be devoted to the form in the following section.

Accepting the form of equation (4.2.6.) we can now write down the cellular expansion corresponding to the equation (2.4.1.) of Chapter 2 in the spherical case. In exactly the same way

$$\begin{aligned}\psi_{\underline{k}}(\underline{r}) &= \sum_L C_L\,\phi_L(\underline{r}) \\ &= \sum_L C_L\Big[\sum_{L'}\mathcal{R}_{L'L}(r)\,Y_{L'}(\hat{\underline{r}})\Big]\end{aligned} \qquad (4.2.8.)$$

The functions $\mathcal{R}_{L'L}(r)$ satisfy the same equation as the $R_L(r)$, viz. equation (4.2.3.), and it would at first appear that the new quantum number, L, is superfluous, as it does not enter explicitly into the equation

$$\frac{1}{r^2}\frac{d}{dr}\Big[r^2\frac{d\mathcal{R}_{L'L}(r)}{dr}\Big] - \Big[\frac{\ell'(\ell'+1)}{r^2} - \epsilon - 2V(r)\Big]\mathcal{R}_{L'L}(r) + 2\sum_{L''}a_{L'L''}(r)\mathcal{R}_{L''L}(r) = 0. \qquad (4.2.9.)$$

However, the initial conditions will provide the necessary L dependence, since at some radius r_o, where the non-spherical corrections commence, the starting values for the solution of the equation (4.2.9.) will be of the form

$$\mathcal{R}_{L'L}(r_o) = R_\ell(r_o)\,\delta_{L',L} \qquad (4.2.10.)$$

and it is not the case that all the $\mathcal{R}_{L'L}(r)$ of given L' have the same value for any L at r_o. The new radial functions thus form a non-trivial square matrix function of r.

The term in square brackets in equation (4.2.8.) can now be calculated at many pairs of boundary points, just as the $[R_\ell(r)\, Y_L(\hat{\underline{r}})]$ in the spherical case, and the usual cellular approach can in principle be employed to fit the wave function to the Bloch condition. There are, however, certain modifications necessary to the standard Cellular Method described in Chapter 2, and we shall return to consider these in Section 4.5. below. We now proceed to relate the form of equation (4.2.6.) for the solutions of the Schrödinger equation to the boundary condition problem of the Cellular Method.

4.3. A Discussion of the New Form of Radial Function.

In this section we attempt to show how the new form of radial function must naturally arise from any attempt to solve the equation (4.2.3.) as it stands. This discussion will also suggest a possible alternative approach to the problem of obtaining the cellular expansion, henceforth referred to as the "iterative approach".

If we were to consider the direct solution of equation (4.2.3.) above, then care would be necessary over the relative sizes of the radial functions used in the coupling term. In the spherical case, the starting values for the solution of equation (2.2.5.) are contained in the series expansions $H_\ell(\rho)$, $Q_\ell(\rho)$, referred to on page 34, which contain an arbitrary factor, later removed by the normalisation condition, since each radial function is independent of all others, and calculated separately. In the non-spherical case, however, the radial functions are coupled together, so that the form of any one radial function in equation (4.2.3.) will depend on the choice of starting values for all the radial functions. To define the problem more precisely, we associate with each radial function, $R_L(r)$,

an arbitrary constant N_L , reflecting this arbitrary factor in the starting value. The wave function of equation (4.2.2.) then becomes

$$\phi(\underline{r}) = \sum_L N_L R_L(r) Y_L(\hat{\underline{r}}) \qquad (4.3.1.)$$

and the radial equation (4.2.3.) takes the form

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR_L(r)}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right]R_L(r) = -\frac{1}{N_L}\sum_{L'} 2a_{LL'}(r)N_{L'}R_{L'}(r) \qquad (4.3.2.)$$

This equation can in principle be solved for any set of constants N_L we might care to choose, and it is quite clear that the radial functions obtained will depend on the choice of N_L made. We now have the choice of either solving the equation (4.3.2.) for different chosen values of the N_L (as is effectively done by Evans and Keller, 1971), or attempting to solve the equation in terms of these constants N_L . We adopt the latter approach here.

Regarding equation (4.3.2.) as an equation for the N_L 's initially, we note that it is both linear and homogeneous in these quantities. We may therefore write a solution in the form

$$N_L R_L(r) = \sum_{L'} \mathcal{R}_{LL'}(r) N_{L'} \quad , \qquad (4.3.3.)$$

and inserting this into equation (4.3.2.) we obtain

$$\sum_{L'}\left\{\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right]\right\}\mathcal{R}_{LL'}(r) N_{L'}$$

$$= -\sum_{L',L''} 2\, a_{LL''}(r)\,\mathcal{R}_{L''L'}(r)\, N_{L'} \quad . \qquad (4.3.4.)$$

Comparing coefficients of N_L on both sides of this equation we obtain finally

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d\mathcal{R}_{LL'}(r)}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right]\mathcal{R}_{LL'}(r) = -2\sum_{L''} a_{LL''}(r)\mathcal{R}_{L''L'}(r) \quad , \qquad (4.3.5.)$$

which is identical to equation (4.2.9.) of the previous section. Thus the

introduction of the linear relation, equation (4.3.3.), for the N_L 's has had the effect of producing an equation for the r-dependent coefficients which is exactly the radial equation of the previous section. Clearly the starting values chosen for the calculation of the $\mathcal{R}_{LL'}(r)$ are unimportant, as they can now be absorbed in the coefficients N_L in the final expression. (We shall show in the following section that it does prove advantageous to choose certain starting values in the calculation of these radial functions.)

Inserting the relation (4.3.3.) into equation (4.3.1.) for the wave function $\phi(\underline{r})$ we obtain

$$\phi(\underline{r}) = \sum_L Y_L(\hat{\underline{r}}) \sum_{L'} \mathcal{R}_{LL'}(r)\, N_{L'} \quad , \qquad (4.3.6.)$$

or rearranging

$$\phi(\underline{r}) = \sum_L N_L \sum_{L'} \mathcal{R}_{L'L}(r)\, Y_{L'}(\hat{\underline{r}}) \quad . \qquad (4.3.7.)$$

Finally, as made clear above, the N_L are arbitrary coefficients, so we may choose them to satisfy the boundary conditions of the problem. This is equivalent to identifying the coefficients with the cellular coefficients, C_L , and on doing this we see immediately that the wave function is identical in form to equation (4.2.8.). We have thus shown how the second set of angular momentum quantum numbers, and the radial function, $\mathcal{R}_{LL'}(r)$, are necessary for the precise solution of the non-spherical radial equation.

This discussion ties up with the relation between the work of Evans and Keller (1971) and that of John et al. (1972) described in Section 1.3. above. The former solve equations analogous to equation (4.2.3.) for the $(\ell_{max} + 1)^2$ radial functions by choosing $(\ell_{max} + 1)^2$ different initial boundary conditions to obtain the sets of solutions

$g_L^i(r)$. This is equivalent here to solving equation (4.3.2.) for $(\ell_{max} + 1)^2$ different sets of coefficients N_L , and the equation (1.3.18.) which takes linear combinations of the solutions $g_L^i(r)$ to obtain the final $\phi_L^k(\underline{r})$ corresponds to equation (4.3.3.) here and hence to the formalism of John et al. Having firmly established the form of equation (4.2.6.), we now proceed to make one further observation on the discussion above which will prove to be the foundation of a possible "iterative approximation" to the solution of the non-spherical problem.

The final step in the above argument - that is to identify the normalisation constants, N_L , with the cellular coefficients C_L suggests another possible approach to the problem. If we try to write down a crystal wave function by applying this argument to equation (4.3.1.) directly we obtain

$$\psi_{\underline{k}}(\underline{r}) = \sum_L C_L R_L(r) Y_L(\hat{\underline{r}}) \qquad (4.3.8.)$$

an expansion which does not in general satisfy the Schrödinger equation, since the individual terms $\left[R_L(r)\ Y_L(\hat{\underline{r}})\right]$ are not solutions. However, if the radial functions $R_L(r)$ of equation (4.3.8.) have been calculated from equation (4.3.2.) with the N_L 's chosen to be identical to the corresponding C_L 's of the cellular expansion, then equation (4.3.8.) will satisfy the Schrödinger equation. Since these C_L 's cannot be found until the cellular calculation has been completed for the given trial energy, some sort of iterative approach, starting from suitably chosen estimates of the C_L 's is suggested, and this is the basis of a new approach to the problem which will be developed in Section 4.6. below. In the context of the work of Evans and Keller this approach is equivalent to calculating a single $g_L^i(r)$

from estimates of the set of boundary conditions which we know must be satisfied by the final wave function, instead of calculating a linearly independent set of $g_L^i(r)$ and forming the appropriate linear combination.

4.4. Solution of the New Radial Equations.

In this section we are concerned with the practical solution of equation (4.2.9.) for the radial functions $\mathcal{R}_{LL'}(r)$, still a coupled set of equations, but with no unknown coefficients involved. Clearly the number of different radial functions has increased drastically from the spherical case - up to a maximum ℓ-value of ℓ_{max} there would be $(\ell_{max} + 1)$ radial functions $R_\ell(r)$ in the spherical case for a general point in $\underline{k}$-space, whereas there are $(\ell_{max} + 1)^4$ of the new radial functions, $\mathcal{R}_{LL'}(r)$. Therefore, in calculating energy levels at general $\underline{k}$-vectors there is an enormous increase in the computing time required, and it is essential that efficient procedures are developed for the solution of the radial equations. (N.B. In the case of a symmetry point in $\underline{k}$-space, the number of radial functions required reduces to the square of the number of independent symmetry adapted harmonics which exist up to ℓ_{max} , and does not represent such a dramatic increase.)

The problem we wish to solve is that of a potential spherically symmetric out to a certain radius, r_o , and with a finite, non-spherical component for $r > r_o$. The problem must, therefore, reduce to the spherical problem for $r \leqslant r_o$, and this has been solved in detail in Section 2.2. The new radial functions, as defined in equations (4.2.6.) and (4.2.9.) must therefore be given by

$$\mathcal{R}_{LL'}(r) = R_\ell(r)\,\delta_{LL'} \quad , \quad r \leqslant r_o \quad , \qquad (4.4.1.)$$

and it is appropriate, in view of the discussion to be presented in the following section immediately after equation (4.5.2.), to normalise the $R_\ell(r)$ used here as they would be in the spherical problem, i.e. the radial functions are first obtained to beyond the equivalent sphere radius, r_e , by omitting the non-spherical part of the potential, so that the normalisation integrals can be calculated. Equation (4.4.1.) defines the starting values required for the numerical solution of equation (4.2.9.) and it is clear that all off-diagonal elements will have zero starting values. The two methods adopted for solution of the spherical case radial equation were the Numerov and Runge Kutta methods, and these can both be adapted for use in the case of the non-spherical problem, though each method will have its specific applications.

In order to use the Numerov method, it is necessary to make an approximation, treating the equation iteratively, starting from the spherical case, with the right hand side of the coupled equation (4.2.9.) considered to contain radial functions from the previous iteration, and therefore a predetermined function of r, L and L' . (This is the approach adopted by Kleinman and Shurtleff (1969), described in Chapter 1.) The substitutions

$$g_{LL'}(\rho) = \mathcal{R}_{LL'}(r)\exp(\tfrac{1}{2}\rho) \quad , \qquad (4.4.2.)$$

$$\rho = \ln(r) \quad , \qquad (4.4.3.)$$

cast equation (4.2.9.) into the form

$$\frac{d^2 g^i_{LL'}(\rho)}{d\rho^2} - \left[(\ell+\tfrac{1}{2})^2 - \{2V(\rho)+\epsilon\}\exp(2\rho)\right] g^i_{LL'}(\rho) \qquad (4.4.4.)$$

$$= -2\sum_{L''} a_{LL''}(\rho)\, g^{i-1}_{L''L'}(\rho)\exp(2\rho) \quad ,$$

where the superscripts on the $g^{i}_{LL'}(\rho)$ are used to indicate the order of the iteration, and

$$g^{0}_{L''L'}(\rho) = R_{\ell''}(r) \exp(\tfrac{1}{2}\rho)\,\delta_{L'',L'} \qquad (4.4.5.)$$

This equation is of the standard form, containing no first derivati ve,

$$y''(x) = F(x)\,y(x) + H(x) \qquad (4.4.6.)$$

which is integrable directly by the method of Numerov (see Hartree, 1958), with starting values given by substituting equation (4.4.1.) into equation (4.4.2.). The number of iterations required to obtain satisfactory convergence will clearly depend on the size of the coupling coefficients $a_{LL''}(\rho)$, and the range $r_o < r \leqslant r_c$ over which they act, where r_c is the radius of the circumscribing sphere of the unit cell. These factors must be considered when deciding upon the best method of solution, for two reasons in particular. Although this method is appreciably quicker to compute than the Runge Kutta method to be described below, the need for several iterations may well alter the situation completely; secondly, it has been found in the past that the Numerov method is not sufficiently accurate when the potential changes rapidly, so that if the radius r_o is small enough for the non-spherical terms to exist near to the atomic nucleus, then this method may not be adequate.

The alternative method of solution becomes apparent if we make the substitution of equation (4.4.3.) along with

$$R_{LL'}(r) = A_{LL'}(\rho) \exp(\ell\rho) \qquad (4.4.7.)$$

and

$$\frac{dA_{LL'}(\rho)}{d\rho} = G_{LL'}(\rho) \quad , \qquad (4.4.8.)$$

which cast equation (4.2.9.) into the form

$$\frac{d\varphi_{LL'}(\rho)}{d\rho} = -(2l+1)\varphi_{LL'}(\rho) - \sum_{L''} b_{LL''}(\rho) H_{L''L'}(\rho) \quad , \qquad (4.4.9.)$$

where we have written

$$b_{LL'}(\rho) = 2\exp[(l''-l+2)\rho]\left\{a_{LL''}(\rho) + [V(\rho)+\tfrac{1}{2}\epsilon]\delta_{L,L''}\right\} \qquad (4.4.10.)$$

Equations (4.4.8.) and (4.4.9.) form simultaneous sets of first order coupled differential equations, and are soluble by the Runge Kutta method (see Section 2.2. above), with starting values at ρ_0 given by equation (4.4.1.) and its derivative.

Clearly, whichever method of solution is employed, the number of functions to be calculated is, as pointed out above, very much larger than in the spherical case. Herein lies the advantage of the iterative approximation to be developed in Section 4.6. below, provided the non-spherical terms are small enough to justify its validity; clearly even a large number of iterations would often be quicker than using the full treatment developed in this section. However, there will be many cases where the present method will be required, and in such cases it will be important to take advantage of as many simplifying and shortening properties as possible. The most important of these is a consideration of the symmetry properties of the lattice, and this will be taken up in the following paragraphs.

The use of symmetry adapted harmonics to reduce the size of the cellular expansion was discussed in Section 2.3. of Chapter 1. There it was pointed out that any wave function expansion may be written as an expansion in the complete set of symmetry adapted harmonics of the appropriate $\underline{k}$-vector, instead of expanding in spherical harmonics. This

technique proves very useful in simplifying the radial equations to be solved in the present case. For, as proved in the discussion on the properties of the coupling coefficients in Section 3.7. of the previous chapter, coupling is only non-zero between functions of the same irreducible representation of the symmetry point. Thus only a fraction of the total possible number of functions will be required to calculate the radial wave functions for one particular representation. The equations to be solved are similar to equation (4.2.9.), if we replace $a_{LL'}(r)$ by $a^{j}_{LL'}(r)$, where j is a combined superscript denoting the symmetry point, representation and column, and the L, L' suffixes are now regarded as numbering the symmetry adapted harmonics with corresponding ℓ-value. These $a^{j}_{LL'}(r)$ are given by equation (3.7.12.) of the previous chapter.

Having obtained the numerical values of the radial functions we are in a position to proceed with the boundary condition fitting. This is described in detail for the spherical case in Chapter 2, and in the following section we shall only deal with those parts which differ from the usual approach.

4.5. Modifications to the Boundary Condition Fitting.

We now return to the form of the cellular expansion presented in equation (4.2.8.). To proceed with the Cellular Method, the quantity in square brackets is calculated at many pairs of boundary points and the Bloch condition and its derivative are fitted to obtain least squares fits to the coefficients C_L , as described in Section 2.4.

The boundary condition problem which, in the form of equations (2.4.7.) and (2.4.8.), now becomes

$$\sum_{L} C_L \sum_{L'} \left\{ R_{L'L}(r_2)\, X_{L'}(\hat{r}_2) - \exp\left[i\underline{k}.(\underline{r}_2-\underline{r}_1)\right] R_{L'L}(r_1)\, X_{L'}(\hat{r}_1) \right\} = 0, \quad (4.5.1.)$$

with a similar expression for the derivative condition, is once again written in the form

$$\sum_{r=1}^{n} A_{sr} x_r = \delta_s \quad , \qquad (4.5.2.)$$

where A_{sr} represents the coefficient of the r-th cellular coefficient, now written x_r , calculated at the s-th point, and the δ_s are a set of residuals, the sum of the squares of which must be minimised, subject to the condition that the cellular expansion must be normalised to unity, i.e.

$$\sum_{r=1}^{n} x_r^* x_r = 1 \quad . \qquad (4.5.3.)$$

The latter normalisation condition arises because the individual radial functions $R_\ell(r)$ are normalised in the spherical case. This is not essential to the method, but doing this ensures that the boundary condition matrix, formed as described in Chapter 2, contains numbers of similar magnitude in all its elements, thus avoiding any possible ill-conditioning in the boundary condition matrix eigenvalue problem. In the present case it should be sufficient, for this purpose, to use starting values for the solution of equation (4.2.9.), at the radius r_o , which are normalised spherical radial functions. This was indeed done in the previous section.

Since the normalisation of the cellular expansion is an integral part of the boundary condition matrix manipulation basic to the Cellular Method, we must consider that here for the expansion of equation (4.2.8.). Consider the integral over the equivalent sphere

$$\int \psi_{\underline{k}}^*(\underline{r})\, \psi_{\underline{k}}(\underline{r})\, d\tau = \sum_{L,L''} C_L^* C_{L''} \sum_{L',L'''} \int Y_{L'}^*(\hat{\underline{r}})\, Y_{L''}(\hat{\underline{r}})\, d\Omega \int \mathcal{R}_{L'L}(r)\, \mathcal{R}_{L'''L''}(r)\, r^2 dr$$

$$= \sum_{L,L''} C_L^* C_{L''} \sum_{L'} \int_0^{r_e} \mathcal{R}_{L'L}(r)\, \mathcal{R}_{L'L''}(r)\, r^2 dr$$

$$= \sum_{L,L''} C_L^* C_{L''}\, m_{LL''} \quad , \qquad (4.5.4.)$$

where

$$\mathfrak{M}_{LL''} = \sum_{L'} \int_0^{r_e} \mathcal{R}_{L'L}(r)\, \mathcal{R}_{L'L''}(r)\, r^2 dr \quad , \qquad (4.5.5.)$$

and we have used the orthonormality of the spherical harmonics in equation (4.5.4.). The required normalisation condition can thus be stated in the form

$$1 = \sum_{L,L'} c_L^* \, c_{L'} \, \mathfrak{M}_{LL'} \qquad (4.5.6.)$$

where the matrix $\underset{\sim}{\mathfrak{M}}$ defined by equation (4.5.5.), is of the type "matrix transposed times matrix" and is therefore symmetric and positive definite. This differs from the usual normalisation condition, expressed in equation (4.5.3.), and in similar notation becomes

$$1 = \sum_{s,r=1}^{n} x_s^* \, \mathfrak{M}_{sr} x_r \qquad (4.5.7.)$$

We shall now work through the boundary condition matrix manipulation with the new constraint and show how this affects the final result. Multiplying equation (4.5.2.) by its complex conjugate gives

$$\sum_{r,u=1}^{n} x_u^* \, A^\dagger_{su} A_{sr} x_r = \delta_s^* \delta_s \quad , \qquad (4.5.8.)$$

and summation over the suffix s gives the required sum of squares of residuals,

$$S^2 = \sum_{s=1}^{2p} \delta_s^* \delta_s = \sum_{r,u=1}^{n} x_u^* \, B_{ur} x_r \qquad (4.5.9.)$$

where $\underset{\sim}{B}$ is defined as the matrix $\underset{\sim}{A}^\dagger \underset{\sim}{A}$ as in Chapter 2. Thus the problem reduces to the minimisation of S^2, given by equation (4.5.9.), subject to the constraint of equation (4.5.7.), and as before is a standard Lagrangian multiplier problem. Following the analysis of Section 2.4. leads to the

equation

$$\sum_{u=1}^{n} x_u^* (B_{ur} - \lambda m_{ur}) = 0 \qquad (4.5.10.)$$

which corresponds to equation (2.4.14.) in the spherical case, where t he m_{ur} is replaced by the Kronecker delta, δ_{ur} . The λ is a Lagrangian multiplier, and is identified, by equation (4.5.9.) with the eigenvalue of the generalised eigenproblem

$$\underset{\sim}{B}\,\underset{\sim}{x} = \lambda\, \underset{\sim}{x} \qquad (4.5.11.)$$

Substituting equation (4.5.11.) into equation (4.5.9.), and using equation (4.5.7.) it is again clear that

$$s^2 = \lambda \qquad (4.5.12.)$$

so that the minimum value of s^2 corresponds to the minimum eigenvalue of the generalised eigenproblem of equation (4.5.11.). Thus, having calculated the new radial functions $R_{LL'}(r)$ and the normalisation matrix elements $m_{LL'}$, the boundary condition fitting can be carried out in much the same way as before, the only difference being the eigenproblem to be solved.

Having established the required eigenproblem, the Cellular Method then proceeds to investigate the properties of the boundary condition matrix $\underset{\sim}{B}$, in order to simplify this eigenproblem. In all but the simplest cases, where the $\underline{k}$-vector being considered is $\frac{1}{2}\underline{K}$, $\underline{K}$ being a reciprocal lattice vector, the boundary condition matrix will be com plex due to the $\exp(i\underline{k}.\underline{T})$ term in each boundary condition. In the spherical case, a powerful theorem, referred to by Altmann (1974) as the "coefficient theorem", can be employed in certain cases described in detail in Section 2.4. and enables $\underset{\sim}{B}$ to be written as a real matrix of the same dimension as the original complex matrix,

In the notation of Section 2.4., with $\bar{\bar{i}}$ and $\bar{\bar{j}}$ respectively inversion and conjugation operators, the coefficient theorem states that, under the conditions given in Section 2.4.,

$$\bar{\bar{i}}\,\psi_{\underline{k}}(\underline{r}) = \bar{\bar{j}}\,\psi_{\underline{k}}(\underline{r}) \quad . \qquad (4.5.13.)$$

Applying this to the symmetrised equivalent of equation (4.2.8.), viz.

$$\psi_{\underline{k}j}(\underline{r}) = \sum_{L} C_L \sum_{L'} \mathcal{R}^{\underline{k}j}_{L'L}(r)\, X^{\underline{k}j}_{L'}(\hat{\underline{r}}) \quad , \qquad (4.5.14.)$$

we obtain respectively, for real harmonics, which is the case for the group O_h ,

$$\bar{\bar{i}}\,\psi_{\underline{k}j}(\underline{r}) = \sum_{L} C_L \sum_{L'} \mathcal{R}^{\underline{k}j}_{L'L}(r)\,(-1)^{\ell'}\, X^{\underline{k}j}_{L'}(\hat{\underline{r}}) \quad , \qquad (4.5.15.)$$

where the radial function is unaffected in a centrosymmetric potential, and

$$\bar{\bar{j}}\,\psi_{\underline{k}j}(\underline{r}) = \sum_{L} C^{*}_{L} \sum_{L'} \mathcal{R}^{\underline{k}j}_{L'L}(r)\, X^{\underline{k}j}_{L'}(\hat{\underline{r}}) \quad . \qquad (4.5.16.)$$

Owing to the sum over L' in the expansion of equation (4.5.14.), there is no simple relation between C_L and C^{*}_{L} as exists in the spherical case, and therefore the simplifications made following the application of this theorem can no longer be made. This results in the boundary condition matrix generally remaining complex, and the solution of the boundary problem becomes consequently more lengthy.

In other than the two respects discussed in this section, the Cellular Method remains unchanged when applied to the new cellular expansion derived here for the non-spherical case. It is worth pointing out at this stage the simplicity with which the non-spherical case can be dealt with by the Cellular Method. The only changes are a different, but similar form of cellular expansion, a generalised matrix eigenvalue problem for the boundary condition, performed, in all but the simplest cases, with a complex matrix. We shall now leave this full treatment of

the non-spherical problem, and consider the iterative approximation suggested in Section 4.3. above.

4.6. An Iterative Approximation to the Non-Spherical Problem.

It is, at this stage, apparent that, despite the simplicity of the complete non-spherical treatment, the increase in computing time necessary to solve the problem in this way will be enormous. As well as the increased number of radial equations to be solved, there is also the enlarged boundary condition matrix, now in general complex, to be dealt with. The method to be developed in this section, like the less accurate approach presented in the Appendix, uses radial functions with only one set of angular momentum quantum numbers, and the same form of cellular expansion as is used in the spherical case, and therefore involves none of the problems encountered in the previous section.

As suggested in Section 4.3., it should be possible to solve equation (4.3.2.) iteratively if a suitable choice of N_L 's can be made to start the process. It was established in that section that the normalisation coefficients, N_L , can be identified with the cellular expansion coefficients, C_L . Since it is necessary, when solving the non-spherical problem to have the radial functions corresponding to the spherical part of the potential, it would seem reasonable to use these functions to calculate also the C_L 's of the spherical part, and to use these as a first estimate of the N_L 's in equation (4.3.2.). With this choice of N_L 's , a new set of radial functions results from the solution of the non-spherical problem, and these can be used to find the next set

of cellular expansion coefficients, C_L. This process is repeated to convergence. We can write this formally as the solution of the equation

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR_L^i(r)}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right] R_L^i(r)$$

$$= -\frac{1}{N_L^{i-1}} \sum_{L'} 2a_{LL'}(r)\, N_{L'}^{i-1} R_{L'}^i(r) \,, \qquad (4.6.1.)$$

where i is the number of iterations performed and the N_L^o are taken to be the C_L's of the spherical case.

Before solving this equation, it is important to study the character of the set of coefficients, C_L. We should expect these cellular expansion coefficients to be small for larger ℓ, being close to unity only for the ℓ-values which appear in the atomic configuration. Typical sets of C_L's for some representations of the point group O_h are as follows:

Table 4.6.1.

The First Six Cellular Expansion Coefficients for Crystal Wave Functions Symmetry Adapted to Representations of O_h

Representation \ Index	1	2	3	4	5	6
ΓA_{1g}	0.999996	9.81×10^{-4}	2.45×10^{-3}	-8.66×10^{-4}	-1.33×10^{-4}	-3.13×10^{-4}
XE_g	-0.998807	3.37×10^{-2}	-1.67×10^{-2}	8.75×10^{-3}	-1.90×10^{-2}	-2.11×10^{-2}
LE_g	-6.26×10^{-1}	-7.78×10^{-1}	-5.03×10^{-2}	5.79×10^{-3}	1.67×10^{-2}	2.05×10^{-3}

Clearly when calculating the radial function corresponding to a non-dominant L-value in the cellular expansion, the coupling with that of dominant

L-value will be considerably enhanced, since, in this case the N_L, will be of order unity, whilst the denominator, N_L may be of order 10^{-2} to 10^{-4}. The result is that the change in some of the radial functions will not be small. This may cause convergence problems, and will have to be fully investigated by calculation.

The most appropriate method for the solution of equation (4.6.1.) would seem to be the approach employed in Section 4.4., described before equation (4.4.2.), choosing the $R_L^i(r)$ on the right of equation (4.6.1.) to come also from the previous iteration, so that the equation is effectively decoupled, becoming

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{dR_L^i(r)}{dr}\right] - \left[\frac{\ell(\ell+1)}{r^2} - \epsilon - 2V(r)\right]R_L^i(r)$$

$$= -\frac{1}{N_L^{i-1}}\sum_{L'} 2\,a_{LL'}(r)\,N_{L'}^{i-1}R_{L'}^{i-1}(r) \quad . \qquad (4.6.2.)$$

This form also has the advantage of always building up the radial wave functions from their values at the previous iteration, rather than from the spherical case, and should improve convergence. It should be noted here that within the iteration loop on the cellular coefficients there will be a further loop on the radial functions corresponding to that required in equation (4.4.4.) above because of the decoupling approximation.

Before leaving this method we should stop to consider what kind of an approximation we are making here, and therefore how good we should expect the results to be. To do this, consider the radial function written in the form

$$R_L(r) = R_\ell(r) + p_L(r) \quad . \qquad (4.6.3.)$$

On the first set of iterations we use the cellular coefficients and radial functions of the spherical case on the right hand side of equation (4.6.2.)

to obtain the new radial functions. These functions are those of the spherical case, corrected by amounts $\rho_L(r)$, and therefore this step should be equivalent to a second order perturbation estimate. Further iterations on the cellular coefficients should improve this estimate, so that the final results should be appreciably more accurate than second order perturbation theory.

First order perturbation results have also been calculated for the non-spherical corrections considered in this work, and a comparison of these with those results obtained from the methods developed in this chapter is presented in Chapter 6.

4.7. Summary.

The techniques necessary for the calculation of band structures when the potential within the crystal unit cell is not spherical have now been fully developed, and an approximation proposed which, if successful, will avoid the enormous increase in computing time necessary to effect the full treatment. The following chapter will describe the various programs necessary to perform such calculations, paying particular attention to the new programs which have had to be written in order to apply these methods, as opposed to the spherical approach. In Chapter 6, the methods developed in this chapter will be applied to the small correction to the Cellular Method, as discussed in Chapters 1 and 3, and the results of the different methods of calculation compared.

Appendix - A Second Approximate Approach to the Non-Spherical Problem.

It was shown in Section 3.5. of Chapter 3, and discussed further in the opening Sections of Chapter 4, that the solution of the Schrödinger equation in the case of a non-spherical potential is not separable into radial and angular parts, the solution being of the form

$$\phi(\underline{r}) = \sum_L R_L(r)\, Y_L(\hat{\underline{r}}) \quad . \qquad (A.1.)$$

The individual function

$$\phi_L(\underline{r}) = R_L(r)\, Y_L(\hat{\underline{r}}) \qquad (A.2.)$$

are therefore not themselves solutions of the Schrödinger equation so that the cellular expansion trial function, if written in similar form to the spherical case, as

$$\psi(\underline{r}) = \sum_L C_L\, R_L(r)\, Y_L(\hat{\underline{r}}) \qquad (A.3.)$$

is not in general a solution of the Schrödinger equation. The work of Chapter 4 has shown how this problem can be overcome, but we shall persist with the form quoted here.

In many important cases in the past it has proved possible to obtain reasonable solutions to problems by using a trial function which is not a solution of the Schrödinger equation in a variational calculation of the energy values (such methods have been applied to the calculation of energy levels in molecules). The Cellular Method has been shown to be equivalent to a Ritz variational procedure (Kohn, 1952), and therefore we ought to be able to obtain some kind of solution to the problem in this way. Evans and Keller (1971), in their work described in Chapter 1 of this thesis, use a trial function in their APW technique

which is not a solution of the Schrödinger equation, and this is shown to lead to an extra term in the variation, and hence in the secular determinant to be solved. The equivalent of this extra term in the Cellular Method would be to do a further boundary condition fit, requiring that the Schrödinger equation be obeyed on some surface (which could conveniently be chosen to be the Wigner-Seitz cell). This would require much change to the Cellular Method, and we believe that the iterative approximation proposed in Section 4.6. is more worthwhile than spending the time on this modification. However, we shall proceed without this extra requirement and the results will be presented in Chapter 6, and compared with those of the more well-founded methods described in Chapter 4.

The radial equation to be solved in order to obtain the set of functions $R_L(r)$ of equation (A.2.) is identical to equation (4.2.3.) above. In order to obtain a normalised set of radial functions, we assume all functions in the equation to be normalised,(i.e. $N_L = 1, \forall L$), and the equation can most conveniently be solved in the same way as described in equations (4.4.2.) to (4.4.4.) above, except that the radial function now has only one set of quantum numbers, L. The set of functions so obtained is used in the cellular expansion, equation (A.3.), and the Cellular Method proceeds as usual.

In conclusion we should point out that, although this method is the simplest of all to apply, there are flaws in the foundation of the method. Accepting that the cellular expansion is not a solution of the Schrödinger equation, we are then free to choose the set of $R_L(r)$ in any way we please. This is apparent from the discussion of Section 4.3., and it is clear that by choosing normalised radial functions in the

coupling terms of equation (4.2.3.) we are effectively choosing the N_L 's introduced into this equation in Section 4.3. without regard for the boundary conditions. We should not, therefore, expect the method to give very accurate results. The results obtained on applying this method to the non-spherical problem developed in Chapter 3 are presented in Tables 6.4.4., 6.4.6. and 6.4.7.

CHAPTER 5

THE COMPUTER PROGRAMS

5.1. Introduction.

In this chapter we shall be concerned with the suite of computer programs necessary to undertake the calculation of band energies by the methods expounded in the earlier chapters. Some of these programs will be identical to those used in the spherical band structure calculations undertaken in the past, and will not be dealt with in much detail; others, however, are either completely new, or vastly modified, and it is these programs which will concern us most in this chapter. The flow diagram presented in Figure 5.1.1. shows how the various programs fit together to compute the band energies, and also gives a brief indication of the purpose of each of the programs.

The GEOMETRY and HARMONICS programs are in principle the same as those used in previous work, though they have been rewritten, and many alterations made to increase their efficiency; these programs need be run only once for any one lattice type, and the programs used for this work have been set up for the f.c.c. lattice. The POTENTIAL program will vary in content depending on the type of work being done. It may be necessary to calculate a full, superposed, non-spherical potential using the method developed in Section 3.2., or in the other extreme, merely to interpolate a given potential onto the radial grid used in the later programs as is the case in the present work where the potential of Chodorow (1939) as presented by Burdick (1963) is employed to compute band energies in copper.

The COUPLING COEFFICIENT programs are completely new, since they represent the essence of the correction to the radial wave functions necessary due to the inclusion of the non-spherical potential as a correction to the cellular method. In the description of these programs, we attempt to generalise the discussion in order to make it relevant no matter how the

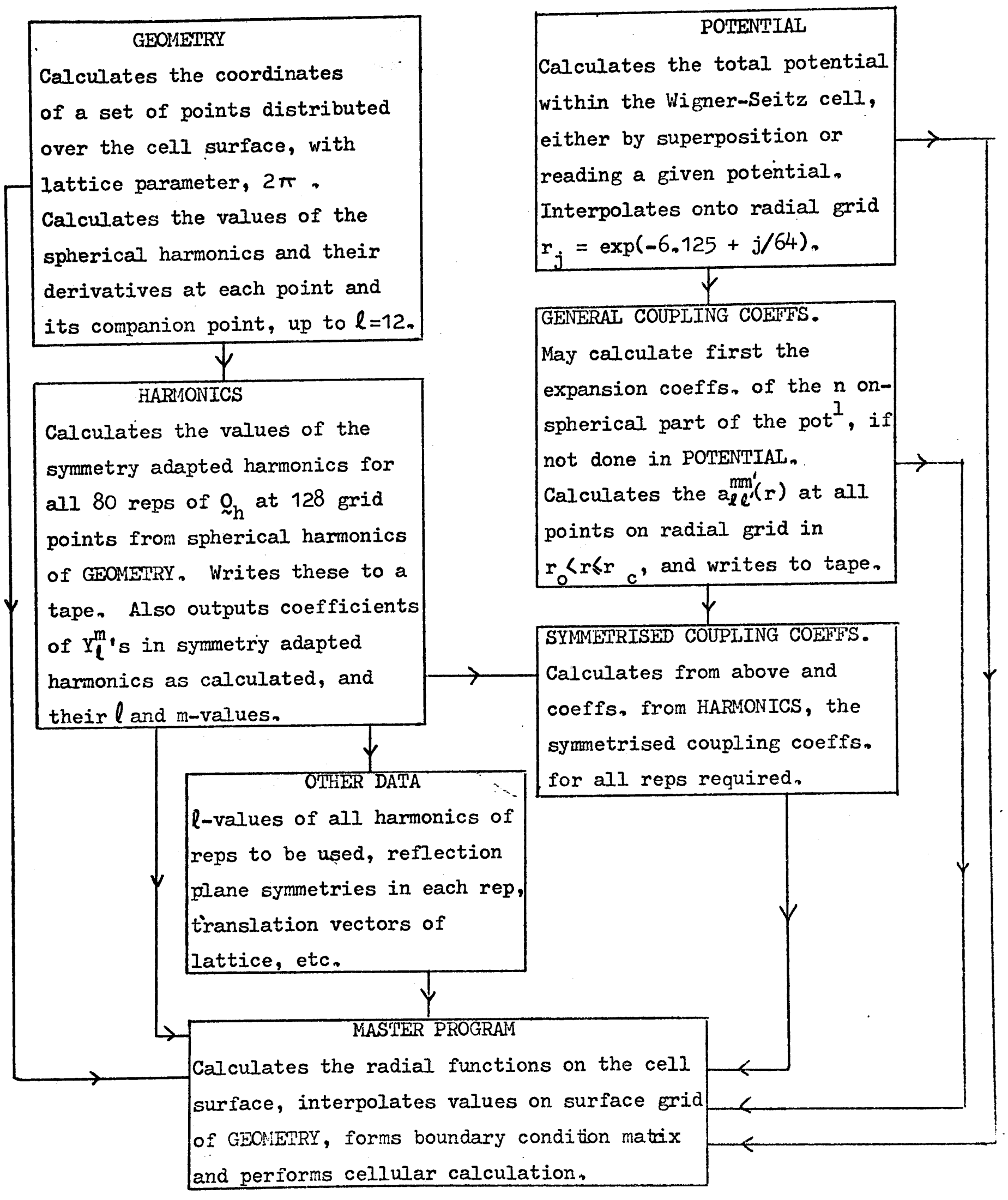
non-spherical potential should arise. The number of coupling coefficients to be calculated is in general very large, though the program has only to be run once for any particular potential field and the time taken for the calculation is not, therefore, a major problem.

The MASTER program, which collects information either directly, or indirectly from all the other programs and performs the actual band energy calculations is very important, in that the enormous increase in number of radial functions to be calculated for the non-spherical case, as pointed out in Chapter 4, makes this program very much more time consuming than before. It is therefore important that all the most efficient procedures are chosen, and that the program is organised and written very carefully; even the "iterative approximation" and "second approximation" techniques require more loops through large parts of the program, in particular the radial integrations procedure. This has resulted in several changes being made in the strategy of the MASTER program, apart from those necessary due to the new form of radial function, and these changes will be indicated in the relevant section.

All programmes are available in full, written in ALGOL for an ICL 1906A machine with GEORGE 3 control, though conversion to FORTRAN for the CDC 7600 machine is at present in progress.

5.2. The GEOMETRY Program.

This program is written generally for any crystal with an f.c.c. structure, for which the Wigner-Seitz cell is a dodecahedron, with each face a rhombus, as shown in Figure 3.4.1. The lattice parameter is taken as 2π , as all results may be multiplied by a suitable scaling

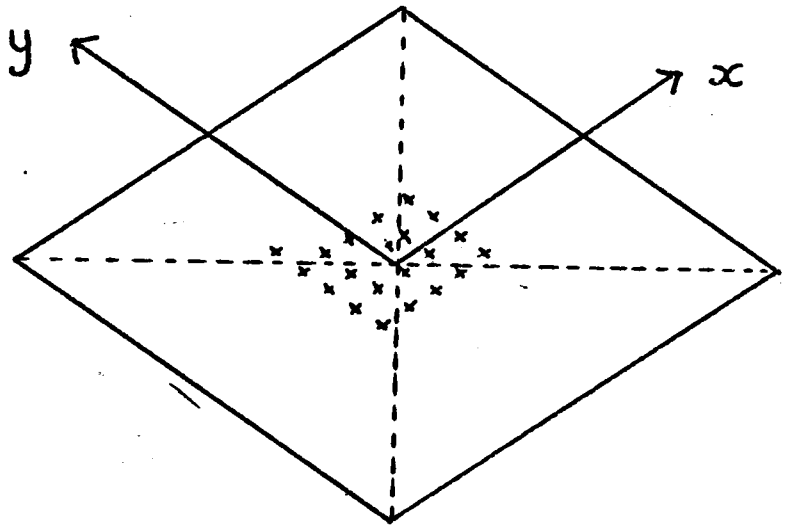


Sequence of Programs for Band Structure Calculations in Non-Spherical Potentials

Figure 5.1.1.

factor at the final stage - this is done in the MASTER program. We shall present here the essential points of the program, for, although the methods employed here have been suggested in the past by workers in this group (see A. R. Harford, 1972), the grid of points has not in fact been programmed in this way before, and some trouble was experienced due to the inclusion of points on symmetry lines. We also take the opportunity to define precisely the spherical harmonics used in this work.

The first task is to spread a grid of points over the boundary in such a way that the points related by symmetry are not included, that points on lines of symmetry and cell edges are excluded, and that there is an even spread of points over the twelve faces. This is best done as shown in Figure 5.2.1., by first considering one face, and constructing on



Construction of a set of General Points on the Cell Surface

Figure 5.2.1.

it, with reference to the non-orthogonal coordinate system shown, a spiral starting at some point near to the centre but away from the axes and the lines $y = \pm x$. If the spiral is built up systematically to contain

256 points, and to approach as near as possible all edges of the rhombus, then all the lines and points of symmetry will be avoided. In order to obtain a grid spread over the entire cell, the following well established procedure is adopted:

(i) the symmetry operations which take face 1 into each of the other eleven faces are assembled;

(ii) the spherical coordinates of the points of the spiral on face 1 are obtained relative to the centre of the cell;

(iii) the first four points remain on face 1, the second four are rotated onto face 2 by the appropriate operator, the third set to face 3, etc. until the thirteenth set will once again remain on face 1, and the cycle is repeated (the faces have a pre-arranged numbering, so that face 1 is opposite to face 7, face 2 opposite to face 8, etc.);

(iv) corresponding to each point, a companion point on the opposite face, obtained by adding the appropriate lattice translation vector, is generated, and for each pair of points, the spherical coordinates and direction cosines of the surface normals at these points are calculated.

The second part of the program uses this information to calculate the spherical harmonics and their normal derivatives up to $\ell = 12$ for each point and companion point. These are generated using the standard recurrence relations for the normalised associated Legendre polynomials, as may be found for instance in Edmonds (1960) [it should, however, be noted that Edmonds includes in his definition of the spherical harmonics the Condon and Shortley (1935) phase factor $(-1)^m$ for $m > 0$, which we do not include in the present work].

The exact relations used are listed below for convenience:

$$P_0^0(\cos\theta) = 1/\sqrt{(4\pi)}\,, \tag{5.2.1.}$$

$$P_{\ell+1}^{\ell+1}(\cos\theta) = \sqrt{\left(\frac{2\ell+3}{2\ell+2}\right)}\sin\theta\,.\,P_\ell^\ell(\cos\theta)\,, \tag{5.2.2.}$$

$$P_{\ell+1}^m(\cos\theta) = \sqrt{\left[\frac{(2\ell+1)(2\ell+3)}{(\ell+m+1)(\ell-m+1)}\right]}\cos\theta\,.\,P_\ell^m(\cos\theta) - \sqrt{\left[\frac{(\ell+m)(\ell-m)(2\ell+3)}{(\ell-m+1)(\ell+m+1)(2\ell-1)}\right]}P_{\ell-1}^m(\cos\theta)\,, \tag{5.2.3.}$$

$$\frac{dP_{\ell+1}^m(\cos\theta)}{d\theta} = (\ell+1)\cot\theta\,.\,P_{\ell+1}^m(\cos\theta) - \mathrm{cosec}\,\theta\,.\sqrt{\left[\frac{(2\ell+3)(\ell-m+1)(\ell+m+1)}{(2\ell+1)}\right]}P_\ell^m(\cos\theta)\,, \tag{5.2.4.}$$

whilst the following check is made at $\ell = \ell_{max}$:

$$P_\ell^m(\cos\theta) = \frac{2(m+1)\cot\theta\,.\,P_\ell^{m+1}(\cos\theta)}{\sqrt{[(\ell+m+1)(\ell-m)]}} - \sqrt{\left[\frac{(\ell-m-1)(\ell+m+2)}{(\ell-m)(\ell+m+1)}\right]}P_\ell^{m+2}(\cos\theta)\,, \tag{5.2.5.}$$

for $0 \leqslant m \leqslant (\ell_{max} - 2)$. The Legendre polynomials and their derivatives are then converted to spherical harmonics and their normal derivatives as follows:

$$Y_\ell^0(\theta,\phi) = P_\ell^0(\cos\theta)\,, \tag{5.2.6.}$$

$$Y_\ell^{m,c}(\theta,\phi) = \sqrt{2}\,P_\ell^m(\cos\theta)\,.\cos(m\phi)\,, \tag{5.2.7.}$$

$$Y_\ell^{m,s}(\theta,\phi) = \sqrt{2}\,P_\ell^m(\cos\theta)\,.\sin(m\phi)\,, \tag{5.2.8.}$$

so that

$$\Omega_0\,.\,\nabla Y_\ell^0(\theta,\phi) = \frac{\ell_\theta}{r}\,\frac{dP_\ell^m(\cos\theta)}{d\theta}\,, \tag{5.2.9.}$$

$$\Omega_0\,.\,\nabla Y_\ell^{m,c}(\theta,\phi) = \frac{\ell_\theta}{r}\sqrt{2}\,\frac{dP_\ell^m(\cos\theta)}{d\theta}\cos(m\phi) - \frac{\ell_\phi\, m}{r\sin\theta}\sqrt{2}\,P_\ell^m(\cos\theta)\sin(m\phi)\,, \tag{5.2.10.}$$

$$\Omega_0\,.\,\nabla Y_\ell^{m,s}(\theta,\phi) = \frac{\ell_\theta}{r}\sqrt{2}\,\frac{dP_\ell^m(\cos\theta)}{d\theta}\sin(m\phi) + \frac{\ell_\phi\, m}{r\sin\theta}\sqrt{2}\,P_\ell^m(\cos\theta)\cos(m\phi)\,. \tag{5.2.11.}$$

The values of these quantities at each point and its companion point are stored together with the point number, face number, radial coordinate and radial direction cosine of normal to the face at each pair of points.

5.3. The HARMONICS Program.

This program produces, for each pair of points on the cell surface (the work of Altmann, Davies and Harford (1968) shows that it is necessary only to use 128 pairs of points provided these are evenly spaced over the whole cell surface), the symmetry adapted harmonics for all representations of the 17 symmetry points in $\underline{k}$-space (80 representations in all), and their normal derivatives. Once calculated, these harmonics are written onto a magnetic tape, stored in groups of representation. The work falls into two parts, viz. the calculation of the harmonics for Γ ($\underline{k} = 0$) which involves 20 representations, and the calculation of the harmonics for the remaining symmetry points in $\underline{k}$-space, which can be derived as linear combinations of the Γ-harmonics, as given for cubic groups by Altmann and Cracknell (1965). This latter stage constitutes the first effort to cut down the size of the MASTER program, which in the past calculated its own harmonics from those of Γ as required when constructing the boundary condition matrix.

The program requires, as its data, most of the coefficients given in the paper of Altmann and Cracknell (1965) in Tables I (a), (c) and (d) and Table IV. The coefficients in Tables I are those of the real spherical harmonics in the symmetry adapted harmonics of all 20 representations of Γ, up to $\ell = 12$, whilst Table IV gives the linear combinations of Γ-harmonics necessary to generate the harmonics of the other symmetry points in $\underline{k}$-space. The theory behind these coefficients is outlined in Section 2.3. of Chapter 2.

The program must calculate, for symmetry points other than Γ, the coefficients of the spherical harmonics appearing in the linear combinations constituting the symmetry adapted harmonics, and since these coefficients are required elsewhere, they too are output to filestore,

before being absorbed into the numerical values of the harmonics. They will later be seen to be necessary in the calculation of the symmetrised coupling coefficients, as well as in perturbation theory estimates of the energy eigenvalues.

5.4. The POTENTIAL Program.

This section is included merely for completeness, since, as mentioned above, the potential used in the work is that used by Burdick (1963), and it is necessary only to interpolate this potential onto the radial grid chosen for the calculation of radial functions, viz.

$$r_j = \exp(-6.125 + j/64) \qquad (5.4.1.)$$

The full non-spherical superposition scheme derived in Chapter 3 is at present being applied to a different problem in this department (C. P. Mallett - private communication), and a description of the necessary programming will be more appropriate there.

5.5. The COUPLING COEFFICIENT Programs.

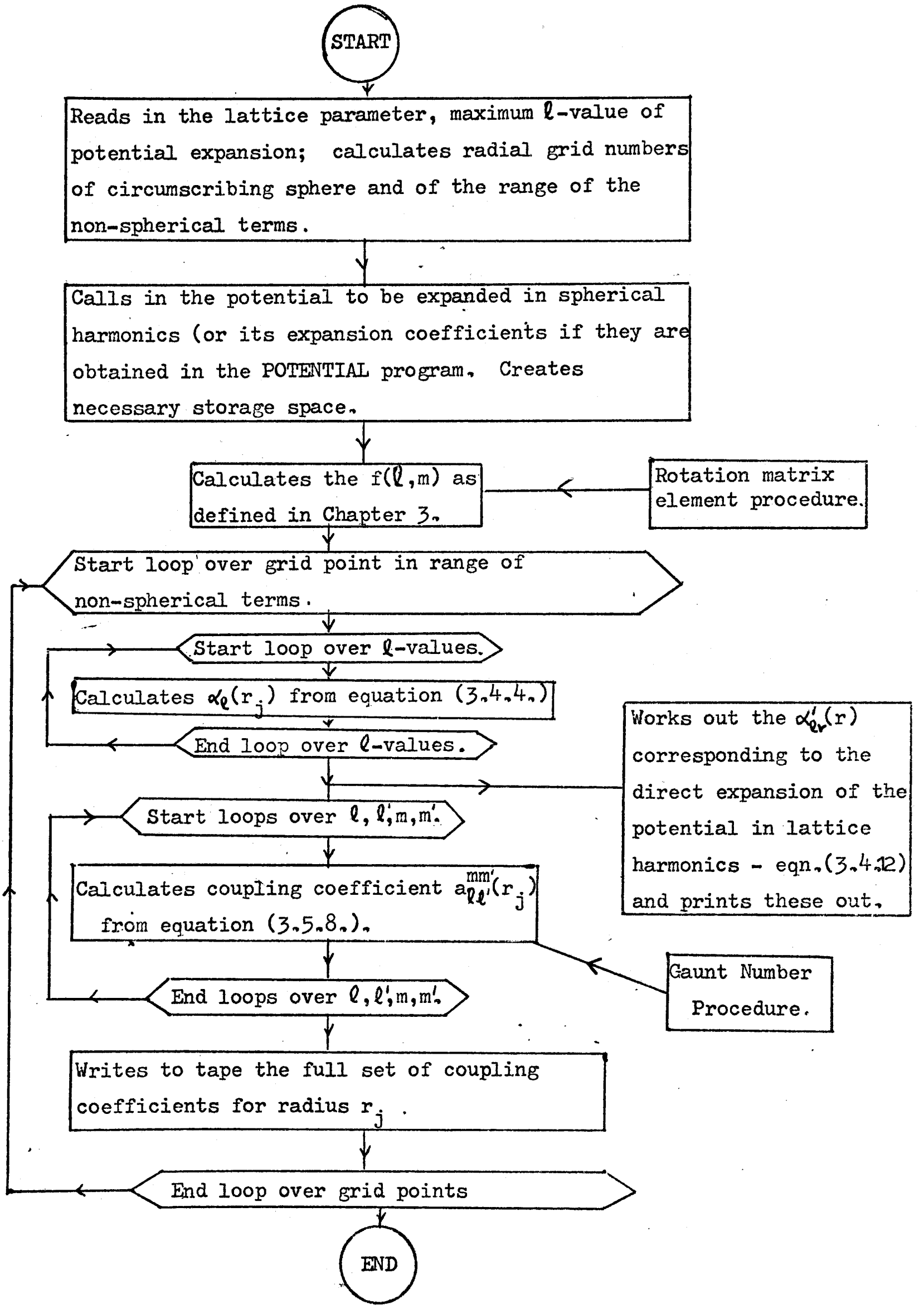
The calculation of the coupling coefficients arising from the inclusion of non-spherical terms in the cell potential is divided into two parts, as shown on the flow diagram of Figure 5.1.1. First the general coefficients, $a_{qq'}^{mm'}(r)$, given by equation (3.5.8.) above must be calculated, and then the coefficients for coupling between radial functions in the symmetry adapted representation, $a_{LL'}^{j}(r)$, are calculated, for use in obtaining the band energies at points of symmetry in $\underline{k}$-space. The programs are, naturally, completely new, and will be described in detail here. The properties of the coupling coefficients discovered in Sections 3.6. and 3.7. of Chapter 3 are used extensively to cut down the number of coefficients,

still extremely numerous, which must be calculated. The flow charts of Figures 5.5.1. and 5.5.2. show how the programs are set up to employ the theory of Chapter 3.

The general COUPLING COEFFICIENT program falls into four distinct parts: the calculation of the $f(\ell,m)$ - the numerical coefficients related to the coefficients used in the symmetry adapted harmonics, and given by equation (3.4.15.) of Chapter 3; the calculation of the expansion coefficients $\alpha_\ell(r)$, if these have not already been calculated in the POTENTIAL program, and given here by equation (3.4.4.); the calculation of the Gaunt numbers; and, finally the summation to give the necessary coupling coefficients. Before going on to discuss these four parts, we ought to expand a little on the calculation of radial grid numbers, performed in the first box of the flow chart. In general, the radii r_c, r_i, r_o, etc. will lie between the points on the radial grid defined by equation (5.4.1.). The calculation performed in the first box produces the number of the grid point immediately below the radius concerned (sometimes, the nearest even grid point below).

The calculation of the $f(\ell,m)$ is a straightforward application of equation (3.4.15.), and requires little further explanation here. It is apparent from this equation that only even ℓ-values, and m-values which are multiples of 4 need to be introduced, and all that is required is the expression for the rotation matrix elements $d^{\ell}_{nm}(\beta)$ given in equation (3.4.16.), and written as a separate procedure in the program.

The expansion coefficients for the potential in the special application considered in this work are calculated by direct integration of equation (3.4.4.) using Simpson's Rule (see, for example, Hartree, 1958), and the upper integration limit given by equation (3.4.5.). The integral is performed on equal steps of the angle θ, where the step is chosen as



General Coupling Coefficient Program Strategy

Figure 5.5.1.

0.005 radians, sufficiently small to give a reasonably accurate integration for even the smallest paths, which are arcs of radius r_j about the central atom, O , between $\theta = 0$ and $\theta = \Theta_{max}$ (see Figure 3.4.1.). An Everett interpolation scheme is used (see again Hartree, 1958) to calculate the potential at points between the radial grid points, necessary in this integrand. The spherical harmonics $Y_\ell^0(\theta,0)$ are easily calculated from the rotation matrix procedure, using the simple relation

$$Y_\ell^0(\theta,0) = \left(\frac{2\ell+1}{4\pi}\right)^{1/2} d_{00}^{\ell}(\theta) \qquad (5.5.1.)$$

deduced, for instance in Chapter 4 of Edmonds (1960). The integration must be repeated for all ℓ-values which have non-zero $f(\ell,m)$ coefficients, and for each point on the radial grid in the range of the non-spherical parts of the potential $r_o < r_j \leqslant r_c$. The resulting $\alpha'_{\ell}(r_j)$ are printed out and studied in order to find a suitable value at which to cut off the expansion of the non-spherical potential.

The calculation of the Gaunt numbers is performed in a separate procedure, called when required by the main program. The Gaunt numbers are defined by equation (3.5.7.), and are given in terms of the Wigner 3-j symbols by the equation

$$\int Y_\ell^{m*}(\hat{r}) Y_{\ell''}^{m''}(\hat{r}) Y_{\ell'}^{m'}(\hat{r}) d\Omega = \left[\frac{(2\ell+1)(2\ell''+1)(2\ell'+1)}{4\pi}\right]^{1/2} \begin{pmatrix} \ell & \ell'' & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & \ell'' & \ell' \\ -m & m'' & m' \end{pmatrix}, \qquad (5.5.2.)$$

where the bracketed six-component symbols are the Wigner 3-j symbols related to Clebsch-Gordon coefficients and discussed in detail by Edmonds (1960). Note, however, that Edmonds's definition of the Gaunt numbers does not include the complex conjugation of the first term in the integrand, and therefore neither the minus sign with the m in the second 3-j symbol. The definition presented here is that of Rotenberg et al. (1959) who present a summary of the properties of the 3-j symbols and also extensive tables

of their numerical values, which proved valuable in making systematic checks of the procedure used in this program. There are many useful recurrence relations available for the calculation of the 3-j coefficients, but since in this application we require only a small selection of the total available coefficients, it proves more economical to calculate each one directly as required. The most general expression, deduced from Edmonds, for the coefficients is:

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \left[\frac{(j_1+j_2-j_3)!(j_2+m_2)!(j_2-m_2)!(j_3+m_3)!(j_3-m_3)!}{(j_1+j_2+j_3+1)!(j_1-j_2+j_3)!(-j_1+j_2+j_3)!(j_1+m_1)!(j_1-m_1)!}\right]^{1/2}$$

$$\times \sum_s (-1)^{s+2j_1-m_1-j_2-m_3} \frac{(j_1+m_1+s)!(j_2+j_3-m_1-s)!}{s!(j_1-m_1-s)!(j_3+m_3-s)!(j_2-j_3+m_1+s)!} \quad , \qquad (5.5.3.)$$

provided $|j_3 - j_2| \leqslant j_1 \leqslant j_2 + j_3$, $|j_1 - j_3| \leqslant j_2 \leqslant j_1 + j_3$, $|j_1 - j_2| \leqslant j_3 \leqslant j_1 + j_2$ and $(m_1 + m_2 + m_3) = 0$; the summation over s is for all values such that the factorials in the denominator of the summand remain non-negative. In the special case of zero m-values, Edmonds quotes the more specialised expression

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{J/2}\left[\frac{(J-2j_1)!(J-2j_2)!(J-2j_3)!}{(J+1)!}\right]^{1/2} \frac{(J/2)!}{(J/2-j_1)!(J/2-j_2)!(J/2-j_3)!}, \qquad (5.5.4.)$$

provided J is <u>even</u>, and the above triangular condition on the j's is satisfied;

$$J = j_1 + j_2 + j_3 \quad . \qquad (5.5.5.)$$

When the conditions quoted are not satisfied the coefficients are zero valued.

The procedure used to calculate the Gaunt numbers consists of a direct application of equations (5.5.2.) to (5.5.5.) with their attendant conditions. Finally we note that both Rotenberg et al. and Edmonds include the Condon and Shortley phase factor, $(-1)^m$ for $m > 0$, in their definition of the spherical harmonics, whereas we remain consistent with

previous work done in the department, using the definitions of Section 5.2. above. It is therefore necessary to take account of this when calculating the Gaunt numbers.

The final step in the program is the construction of the coupling coefficients, $a^{mm'}_{\ell\ell'}(r)$, from their various constituents calculated as described in the foregoing paragraphs. This is a basic application of equation (3.5.8.), though the choice of values of ℓ, ℓ', m, m' for which the coefficients are calculated merits further discussion. In Section 3.6. of Chapter 3 it was shown that there are four broad categories of these general coupling coefficients, each dividing naturally into two further categories, corresponding to the fact that only radial functions with m-values identical when written modulo-4 actually couple. This leads to the existence of eight independent sets of coupled equations to be solved for the radial functions, and it is therefore convenient to have the coupling coefficients corresponding to these eight categories grouped separately, rather than arranged purely in ascending order of ℓ-value and m-value respectively. This approach will save machine time in tape manipulation in the MASTER program, and, in view of the discussion of the Introduction to this chapter, is therefore of vital importance. In view of the extremely large number of coefficients possible, it is also important to ensure that no duplication occurs and that coefficients which are obviously zero are not stored. This entails making full use of the properties derived in Section 3.6. The division into eight, rather than four, categories will eliminate a large number of zero coefficients, whilst equations (3.6.8.) and (3.6.9.) will allow us to cut down further the number of coefficients calculated: it is clearly only necessary to calculate $a^{mm'}_{\ell\ell'}(r)$ for

$$\ell' \leq \ell \quad , \quad m' \geq 0 \quad , \qquad (5.5.6.)$$

in each category, since the remaining coefficients may be deduced immediately from equations (3.6.8.) and (3.6.9.).

These sets of coefficients are obtained for each radial grid point in the range $r_o < r_j \leqslant r_c$, and output to magnetic tape, category by category, point by point, leaving them in the correct order to be called, either for the symmetrised COUPLING COEFFICIENTS program to be described below, or for the MASTER program, where the radial equations are actually solved. We now move on to discuss the program used to generate the symmetrised coupling coefficients, which uses as its starting point the results of the program just described.

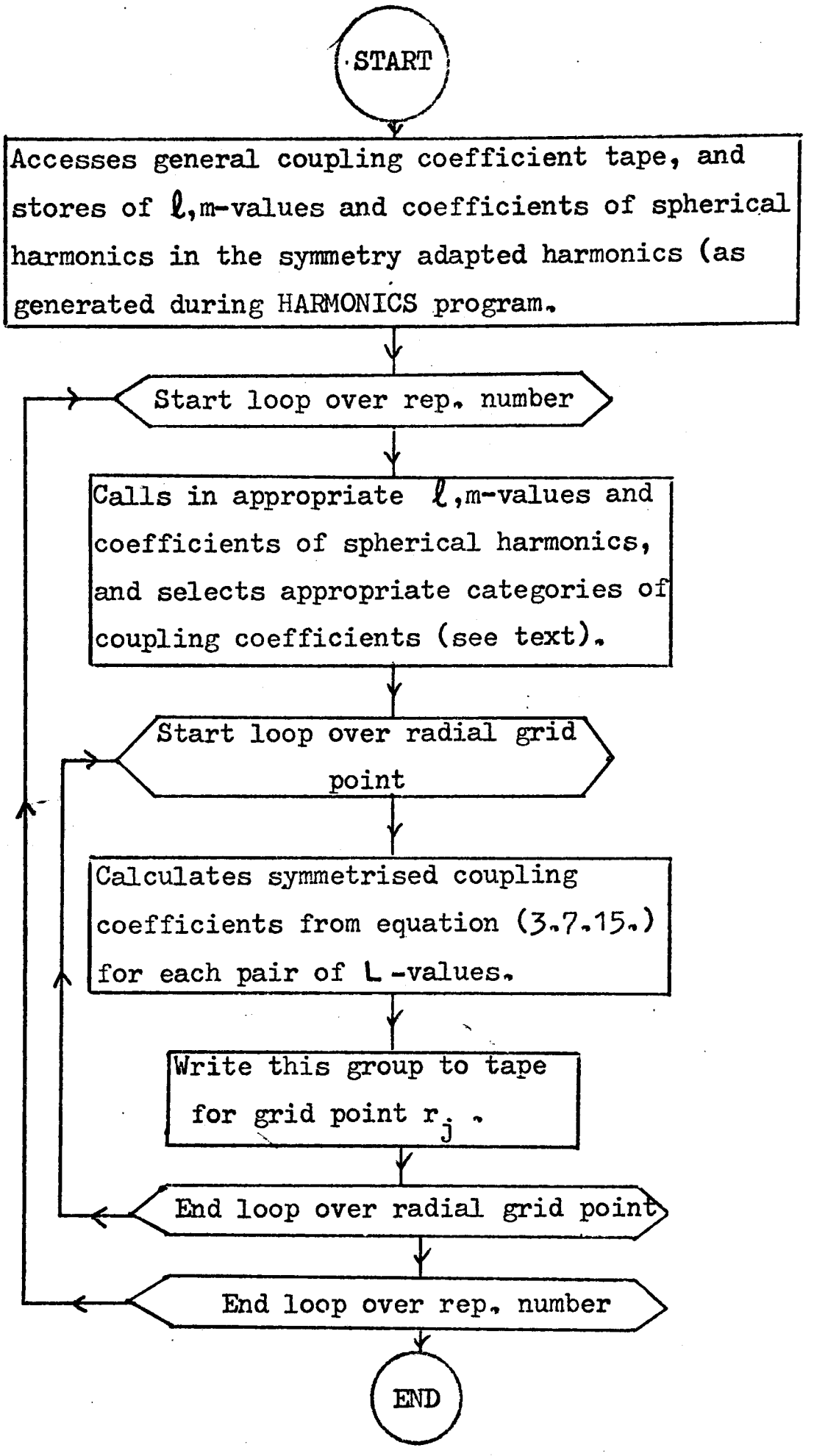
The symmetrised coupling coefficients, $a^j_{LL'}(r)$, are given by equation (3.7.15.) in terms of the general coefficients produced as above. The present program is simply an application of this equation, though the exact expression used is a little tricky to obtain, and the derivation will be presented here. The coefficients of the spherical harmonics in the symmetry adapted harmonics of the required representations are stored as coefficients of the real spherical harmonics $Y_\ell^{mc}(\hat{\underline{r}})$ and $Y_\ell^{ms}(\hat{\underline{r}})$, with $m \geqslant 0$, and thus require conversion. Equation (3.7.15.) for the coupling coefficients,

$$a^j_{LL'}(r) = \sum_{m,m'} A^j_{Lm} A^j_{L'm'} a^{mm'}_{\ell\ell'}(r) \qquad (5.5.7.)$$

may be rewritten as

$$a^j_{LL'}(r) = \sum_{m,m' \geq 0} \left[A^j_{Lm} A^j_{L'm'} a^{mm'}_{\ell\ell'}(r) + A^j_{Lm} A^j_{L'-m'} a^{m-m'}_{\ell\ell'}(r) + A^j_{L-m} A^j_{L'm'} a^{-mm'}_{\ell\ell'}(r) + A^j_{L-m} A^j_{L'-m'} a^{-m-m'}_{\ell\ell'}(r) \right] \qquad (5.5.8.)$$

when we shall have to allow for the fact that this expression includes the terms of zero m-value twice. Therefore, in terms of the coefficients of the real spherical harmonics, which we shall write $B^{jL}_{m\mu}$, the A^j_{Lm} are given by



Symmetrised Coupling Coefficient Program Strategy

Figure 5.5.2.

$$A^j_{Lm} = \begin{cases} B^{jL}_{|m|,u} / \sqrt{2} & m > 0 , \\ B^{jL}_{0,u} / 2 & m = 0 , \\ \pm B^{jL}_{|m|,u} / \sqrt{2} & m < 0 , \end{cases} \qquad (5.5.9.)$$

where the $\pm$ sign refers to a cosine or sine term respectively, that is to $u = c$ and $u = s$. Inserting these into equation (5.5.8.) and using the property of the general coupling coefficients given in equation (3.6.8.), we obtain

$$a^j_{LL'}(r) = \begin{cases} \sum_{\substack{m,m' \geq 0 \\ u = c,s}} \left[B^{jL}_{m,u} B^{jL'}_{m',u'} a^{mm'}_{ll'}(r) \pm B^{jL}_{m,u} B^{jL'}_{m',u'} a^{-mm'}_{ll'}(r) \right] \beta \\ 0 , \text{ if } L \text{ and } L' \text{ have } u \neq u' \text{ throughout expansion.} \end{cases} \qquad (5.5.10.)$$

where

$$\beta = \begin{cases} 1/2 , & m,m' = 0 \\ 1/\sqrt{2} , & m \text{ or } m' = 0 \\ 1 , & \text{otherwise} . \end{cases} \qquad (5.5.11.)$$

Equation (5.5.10.) is the equation used in the program, and it is clear that

$$a^j_{LL'}(r) = a^j_{L'L}(r) . \qquad (5.5.12.)$$

Also used is the property that there is no coupling between expansions which are completely in the real part of the spherical harmonics and those in the imaginary part only. The $a^j_{LL'}(r)$ are calculated for all small representations of the necessary symmetry points and stored on tape, representation by representation, grid point by grid point.

5.6. Other Data.

Again, this section is included merely for completeness, as much of the subsidiary data provided will depend on the type of calculation being performed. Apart from the ℓ-values of all symmetry adapted harmonics of the representation being considered, and the translation vectors of the lattice, the principal information provided under this classification is the reflection plane symmetry data, and we shall explain this in a little more detail.

The reflection plane data is concerned with boundary conditions redundant due to point and companion point being related by a reflection symmetry. As an example consider the symmetry point, Γ, at the centre of the cell; clearly each face and its opposite are related by a reflection symmetry possessed by Γ. Consequently all the boundary conditions will be trivial and only the derivative conditions will give meaningful values. The redundant boundary conditions can be eliminated before they are calculated by making use of the given data, and this is clearly in the interests of time saving in the MASTER program.

5.7. The MASTER Program.

During the course of this work we use three different forms of the MASTER program, corresponding to the methods developed in Sections 4.2., 4.6. and the Appendix respectively of Chapter 4, as well as a first order perturbation theory estimate to be discussed in the following section. The flow chart of Figure 5.7.1. shows the broad strategy of these three approaches, whilst Figure 5.7.2. gives a more detailed break down of the radial equation procedure, placing most emphasis

on the full treatment of the non-spherical problem. The cubic fit to the potential, and the solution of the boundary condition matrix eigenvalue problem are performed by standard library routines, whilst all other steps have been specially programmed. The actual numerical techniques used, viz. Numerov and Runge Kutta integrations, Everett interpolations, Simpson and six-point difference numerical integrations and six point difference differentiation, are in principle the same as those used in the past for calculation of band energies in this group, and we refer to the work of A. R. Harford (1972) for a full description of the cellular program as it stood before this work began.

Apart from much streamlining of the program, the principal alterations made have been in respect of the adaption of the program to deal with radial functions in the symmetry adapted representation, the removal of the calculation of the relevant symmetry adapted harmonics now performed in the HARMONICS program, the generalisation of the boundary condition matrix construction necessary from the discussion of Section 4.5., and the writing of a more involved Runge Kutta routine to deal with simultaneous sets of coupled equations for the radial functions (discussed in Section 4.4.). Disc backing store is required if the large arrays $\mathcal{R}_{LL'}(r)$ are being calculated, and the organisation of this matrix in a linear array is important to the efficiency of the program, which must call these arrays, interpolate values on the cell grid points and then proceed with the matrix $\mathcal{R}_{LL'}(r)$ calculated at the grid point.

The flow diagrams of Figures 5.7.1. and 5.7.2. give as much detail as is possible of the program strategy used to apply the techniques developed in Chapter 4 without actually giving a line by line account of these large programs, and we now pass on to a short discussion

START

Reads in lattice parameter, atomic number, radial grid size, no. of boundary points to be fitted, rep. no., maximum ℓ-value taken in cellular expansion, trial energies. Accesses all required tapes and stores.

Collects ℓ-values of required rep. and calculates size of boundary condition matrix.

Sets flags for reflection plane symmetries of rep. concerned, used below to eliminate redundant boundary conditions. Calculates $\left.\begin{matrix}\sin\\ \cos\end{matrix}\right\} 2\pi \underline{k}.\underline{T}$ for each pair of faces.

Starts loop over boundary points

Collects lattice harmonics of appropriate rep. Collects point and face number, and scales radius of point up from units of 2π using lattice parameter.

Calculates real and imaginary parts of angular parts of boundary conditions, viz.

$$X_\ell(\hat{r}_1) - \cos(\underline{k}.\underline{T})\, X_\ell(\hat{r}_1),$$
$$- \sin(\underline{k}.\underline{T})\, X_\ell(\hat{r}_1), \text{ etc.}$$

Passes these values out to disc backing store

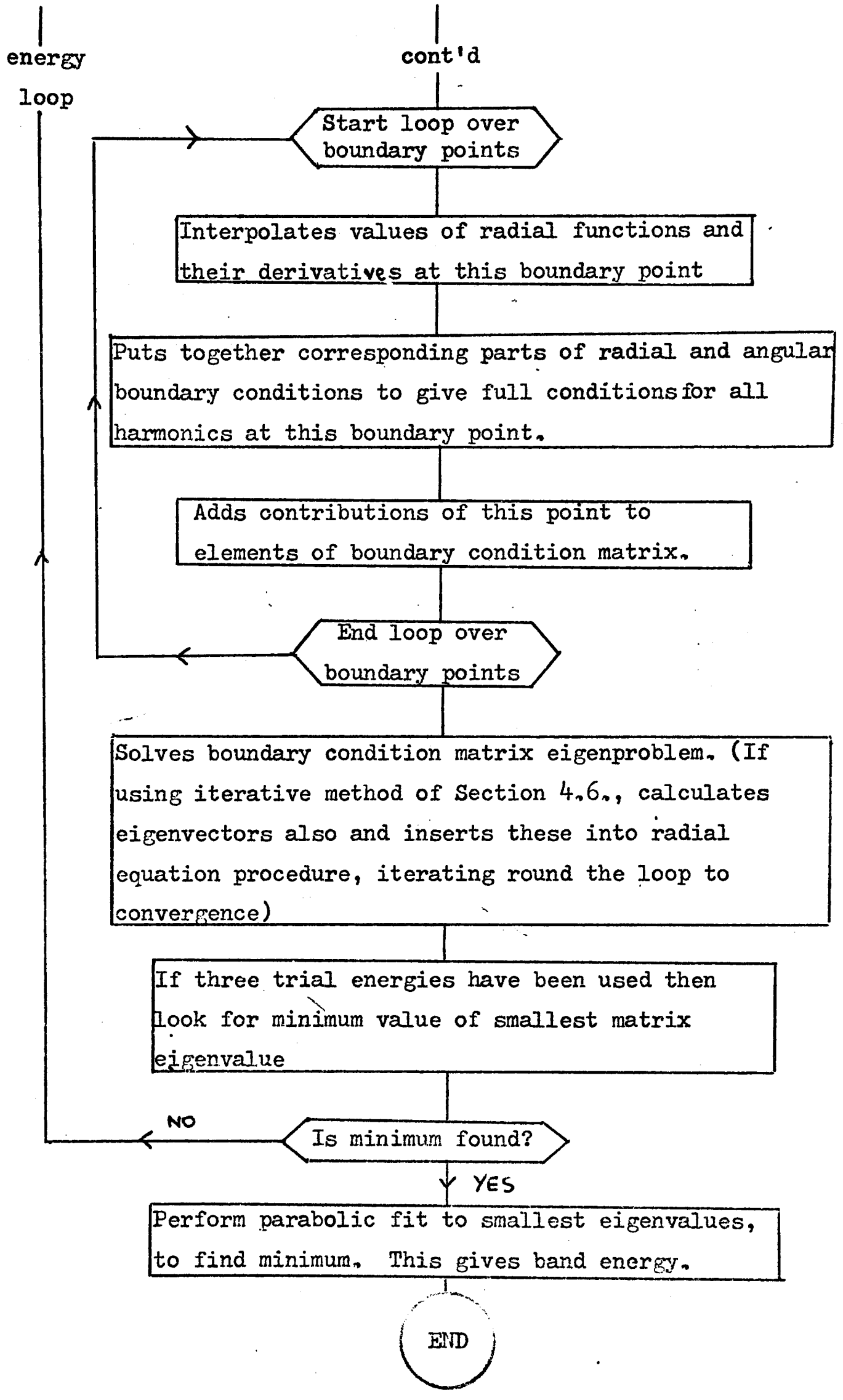
End loop over boundary points

Collects cellular potential, and performs cubic fit to this near the origin.

Start loop over trial energy values

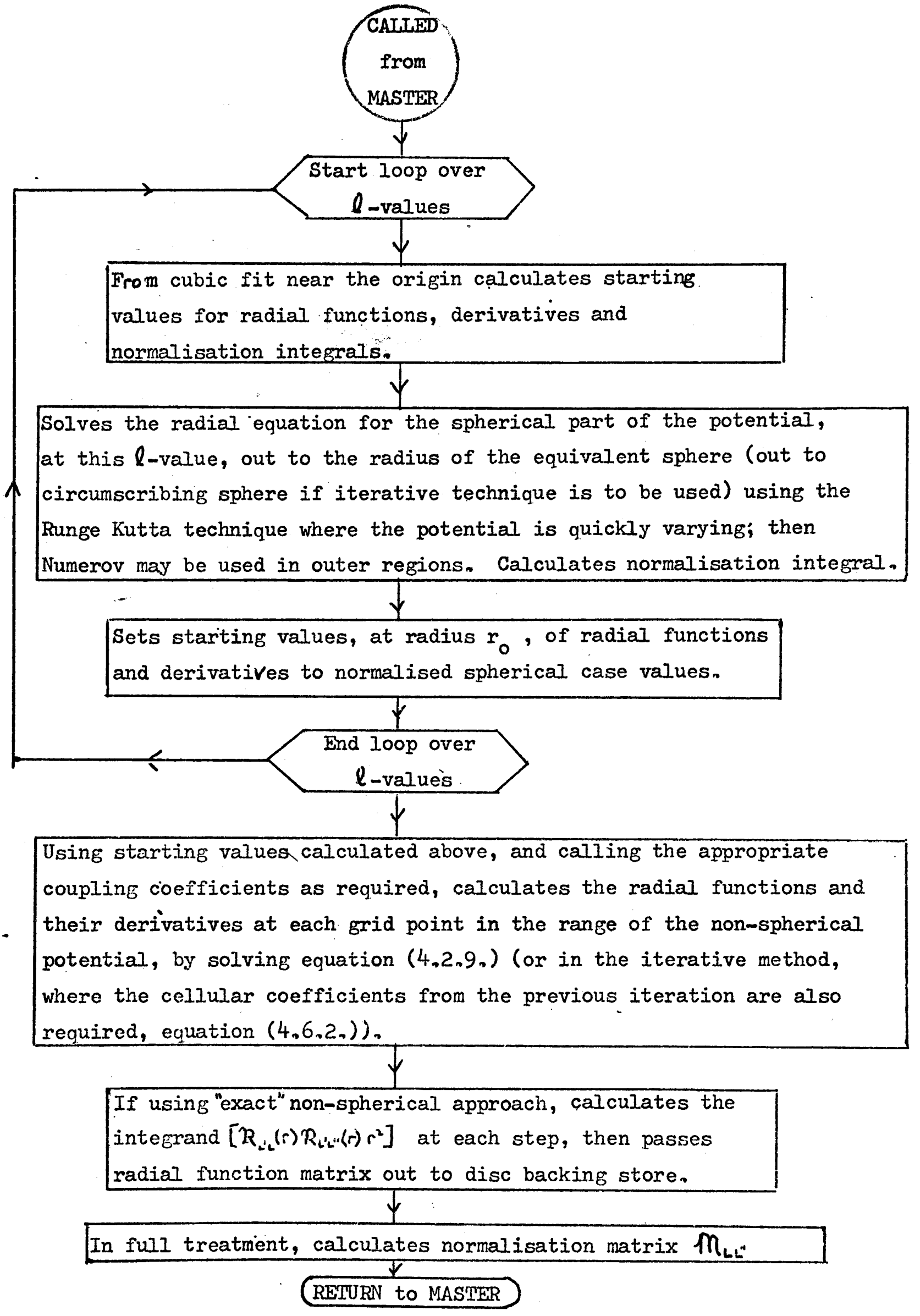
Solves radial equations for given trial energy, passing the values out to disc backing store (see Fig. 5.7.2. for flow chart of this section).

cont'd



Master Program Strategy

Figure 5.7.1.



Radial Functions Procedure

Figure 5.7.2.

of the application of first order perturbation theory to give an estimate of the band energies in the non-spherical problem.

5.8. First Order Perturbation Theory.

There is clearly no reason to discuss the origins of a first order perturbation theory calculation in these pages, and we refer the reader to one of the many suitable treatments of the subject, Merzbacher (1971). Here we shall simply point out how the method is implemented in the case under discussion.

We regard the non-spherical terms in the expansion of the potential given in equation (3.7.2.) of Chapter 3 as a perturbation on the spherical problem, with potential V(r) . In the spherical case, the trial wave function used in the Cellular Method, for symmetry point $\underline{k}$ and small representation j is of the form

$$\psi_{\underline{k}j}(\underline{r}) = \sum_{L} C_L^{\underline{k}j} R_\ell(r) X_L^{\underline{k}j}(\hat{\underline{r}}) , \qquad (5.8.1.)$$

and we now assume that the $C_L^{\underline{k}j}$'s are those calculated at the band energy, so that $\psi_{\underline{k}j}(\underline{r})$ is a wave function in the crystal. In a standard band energy calculation the $C_L^{\underline{k}j}$'s will also have been normalised, so that the first order perturbation theory correction is given by

$$\delta\epsilon = \int \psi^*_{\underline{k}j}(\underline{r}) \sum_{L''} \alpha_{L''}(r) X^{\Gamma A_{ij}}_{L''}(\hat{\underline{r}}) \psi_{\underline{k}j}(\underline{r}) \, d\tau , \qquad (5.8.2.)$$

and inserting the form of the wave function $\psi_{\underline{k}j}(\underline{r})$ and separating into radial and angular integrals, we obtain

$$\delta\epsilon = \sum_{L,L',L''} C_{L'}^{\underline{k}j\,*} C_L^{\underline{k}j} \int R_{\ell'}(r) \alpha_{L''}(r) R_\ell(r) r^2 dr \int X_{L'}^{\underline{k}j}(\hat{\underline{r}}) X^{\Gamma A_{ij}}_{L''}(\hat{\underline{r}}) X_L^{\underline{k}j}(\hat{\underline{r}}) \, d\Omega . \qquad (5.8.3.)$$

The perturbation theory program is a direct application of this equation, and apparently requires similar data to the coupling coefficients program, since the last integral is the familiar integral of three lattice harmonics.

The MASTER program is first run for the spherical case and the band energy obtained; a further run of the program at this band energy produces the coefficients C_L^{kj}. Finally a Gaunt number procedure, and the coefficients of the spherical harmonics in the symmetry adapted harmonic expansions, the B_{mu}^{jL} of Section 5.5. above, provide the information necessary to calculate the final integral, and the expression of equation (5.8.3.) can be evaluated to give the perturbation estimate.

5.9. Summary.

The computational details necessary for the calculation of electron band energies in the case of a non-spherical potential have been gathered together in this chapter. In the final chapter we shall present, and discuss, the results obtained from the various programs written as described above.

CHAPTER 6

RESULTS AND DISCUSSION

6.1. Introduction.

In this chapter we shall present the numerical details of the band energy calculations undertaken on f.c.c. copper, using the non-spherical correction to the Chodorow muffin tin potential as calculated in Chapter 3 above. These calculations are performed for the lower lying representations of the points of high symmetry, Γ , X and L (see Figure 2.3.1.), as chosen by Altmann, Harford and Davies (1968) for their calculations on copper. The band energies are obtained using the three methods developed in Chapter 4 and its Appendix, as well as by first order perturbation theory, using the spherical Chodorow potential as the unperturbed state, and these results are compared. As was emphasised in Section 1.5. of Chapter 1, a check must be kept on the convergence of the cellular expansion, and to this end selected representations are calculated for several maximum ℓ-values in the expansion. The convergence of the iterative treatment with number of iterations on radial solutions and cellular coefficients is also investigated.

We discuss the relation between the results of the spherical approach and those of the non-spherical method applied to the corrections considered here. The small difference between the two sets of results is noted and the significance of this fact in relation to the reliability of the conventional Cellular Method is pointed out. Some discussion of the relative reliability of the two sets of results is presented, supported in the Appendix by a simple illustration.

Finally we discuss the techniques used, and results obtained in relation to the other methods of electron energy band calculation discussed in Chapter 1 above, indicating where techniques developed here might be usefully employed in these other methods, and also indicate the direction in which this research is being pursued at present.

6.2. The Potential.

As stated above, the non-spherical calculations are performed with the Chodorow potential for copper, in the muffin tin form employed by Burdick, as a basis. The reasons for choosing copper for this investigation are discussed in Chapter 1 above. It seems quite clear from the discussion of Connolly (1971) that the variation in results for different methods of calculation on copper is attributable to the different potentials chosen, rather than to the different methods employed. This belief is enhanced by the results of Altmann, Harford and Davies (1968), also for copper. Ballinger and Marshall (1967) also present sets of band energies calculated for selected representations for a variety of different copper potentials, showing the differences obtained in KKR calculations on these potentials. The Chodorow potential is a convenient choice here since it is continuous at the muffin tin sphere, a desirable feature in view of the fact that the Cellular Method solves the Schrödinger equation out to the cell surface in a continuous manner. (Most potentials built up by the prescription of Mattheiss (1964 a) use a flat potential outside the muffin tin sphere which is an average of the superposed potential between the sphere and the cell surface, and therefore not continuous at the sphere.) Our results will also be directly comparable with those of Altmann, Harford and Davies, produced in this department.

In the present calculations we shall not expect to find the results of the non-spherical case varying from the spherical case by nearly so much as the variation shown by Connolly and by Ballinger and Marshall from potential to potential. We cannot, therefore, hope to contribute towards an improvement of the results compared to the experimental results obtained from the optical photoemission measurements

Table 6.2.1.

Chodorow's Potention Energy for Copper

Potential = -2Z(r)/r Rydbergs

r a.u.	2Z(r)	r	2Z(r)	r	2Z(r)
0.000	58.000	0.280	25.462	1.02	6.567
0.005	57.500	0.300	24.264	1.10	5.963
0.010	52.206	0.340	22.186	1.18	5.429
0.015	54.966	0.350	21.723	1.20	5.310
0.020	53.797	0.380	20.470	1.26	4.983
0.025	52.688	0.400	19.660	1.30	4.778
0.030	51.644	0.420	18.851	1.34	4.573
0.035	50.656	0.450	17.678	1.40	4.284
0.040	49.720	0.460	17.308	1.42	4.197
0.050	47.970	0.500	15.965	1.58	3.594
0.060	46.358	0.540	14.772	1.60	3.533
0.070	44.849	0.550	14.488	1.74	3.183
0.080	43.420	0.580	13.625	1.80	3.066
0.090	42.060	0.600	13.128	1.90	2.874
0.100	40.755	0.620	12.631	2.00	2.724
0.120	38.333	0.660	11.680	2.06	2.635
0.140	36.140	0.700	10.874	2.20	2.468
0.160	34.157	0.780	9.408	2.22	2.446
0.180	32.359	0.800	9.099	2.38	2.293
0.200	30.741	0.860	8.252	2.40	2.277
0.220	29.276	0.900	7.782	2.41	2.270
0.240	27.917	0.940	7.312	2.60	2.441
0.260	26.662	1.00	6.749	2.80	2.629

Lattice Parameter = 6.83087 a.u.

Muffin Tin Radius = 2.4151 a.u.

Potential outside Muffin = 0.939 Rydbergs.

Nearest grid point below muffin radius = 448

Nearest grid point below circumscribing sphere radius = 470

Table 6.2.2.

Non-Zero Coefficients for Non-Spherical Correction

to Chodorow Muffin Tin Potential in Expansion

$$V_c(\underline{r}) = \sum_{\ell} \alpha'_\ell(r) X_\ell^{[A_{1g}]}(\hat{\underline{r}})$$

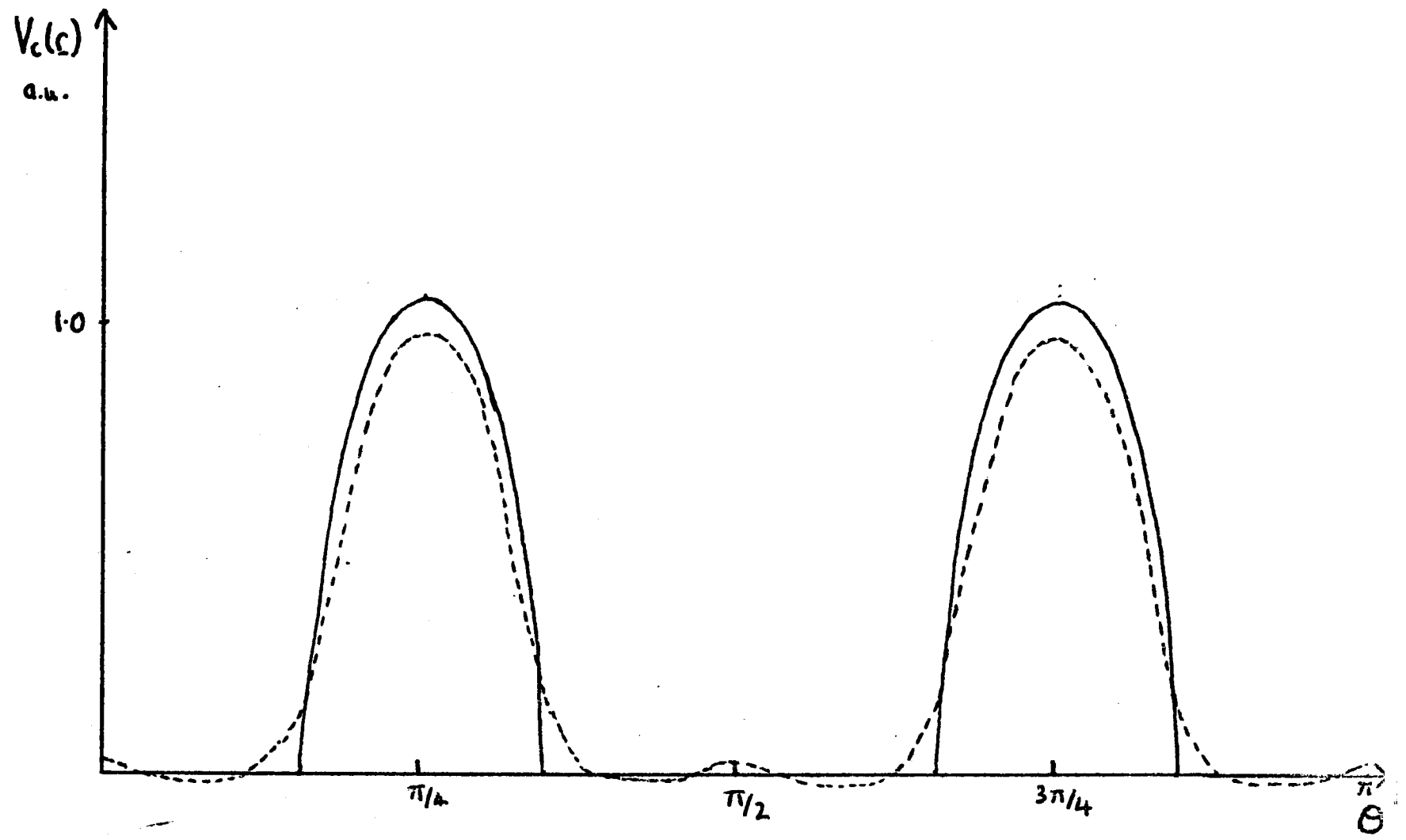
grid no. j	$\alpha_0(r_j)$	$\alpha_4(r_j)$	$\alpha_6(r_j)$	$\alpha_8(r_j)$	$\alpha_{10}(r_j)$	$\alpha_{12}(r_j)$
449	7.410×10^{-4}	4.175×10^{-4}	1.482×10^{-3}	1.162×10^{-3}	3.980×10^{-5}	1.948×10^{-3}
450	5.255×10^{-3}	2.894×10^{-3}	1.002×10^{-2}	7.580×10^{-3}	2.481×10^{-4}	1.147×10^{-2}
451	1.456×10^{-2}	7.836×10^{-3}	2.642×10^{-2}	1.928×10^{-2}	6.009×10^{-4}	2.609×10^{-2}
452	2.889×10^{-2}	1.518×10^{-2}	4.983×10^{-2}	3.496×10^{-2}	1.033×10^{-3}	4.176×10^{-2}
453	4.792×10^{-2}	2.466×10^{-2}	7.900×10^{-2}	5.349×10^{-2}	1.504×10^{-3}	5.669×10^{-2}
454	7.256×10^{-2}	3.654×10^{-2}	1.141×10^{-1}	7.440×10^{-2}	1.981×10^{-3}	6.897×10^{-2}
455	1.023×10^{-1}	5.049×10^{-2}	1.540×10^{-1}	9.689×10^{-2}	2.447×10^{-3}	7.841×10^{-2}
456	1.376×10^{-1}	6.662×10^{-2}	1.986×10^{-1}	1.259×10^{-1}	2.885×10^{-3}	8.453×10^{-2}
457	1.787×10^{-1}	8.496×10^{-2}	2.479×10^{-1}	1.453×10^{-1}	3.295×10^{-3}	8.771×10^{-2}
458	2.255×10^{-1}	1.055×10^{-1}	3.015×10^{-1}	1.715×10^{-1}	3.694×10^{-3}	8.919×10^{-2}
459	2.794×10^{-1}	1.286×10^{-1}	3.603×10^{-1}	1.986×10^{-1}	4.065×10^{-3}	8.849×10^{-2}
460	3.392×10^{-1}	1.539×10^{-1}	4.236×10^{-1}	2.269×10^{-1}	4.423×10^{-3}	8.632×10^{-2}
461	4.064×10^{-1}	1.817×10^{-1}	4.915×10^{-1}	2.559×10^{-1}	4.751×10^{-3}	8.244×10^{-2}
462	4.805×10^{-1}	2.122×10^{-1}	5.653×10^{-1}	2.872×10^{-1}	5.109×10^{-3}	7.942×10^{-2}
463	5.626×10^{-1}	2.457×10^{-1}	6.458×10^{-1}	3.211×10^{-1}	5.502×10^{-3}	7.761×10^{-2}
464	6.529×10^{-1}	2.822×10^{-1}	7.328×10^{-1}	3.573×10^{-1}	5.921×10^{-3}	7.645×10^{-2}
465	7.516×10^{-1}	3.219×10^{-1}	8.267×10^{-1}	3.961×10^{-1}	6.378×10^{-3}	7.636×10^{-2}
466	8.596×10^{-1}	3.653×10^{-1}	9.292×10^{-1}	4.390×10^{-1}	6.916×10^{-3}	7.936×10^{-2}
467	9.780×10^{-1}	4.129×10^{-1}	1.042×10^{0}	4.873×10^{-1}	7.580×10^{-3}	8.717×10^{-2}
468	1.107×10^{0}	4.653×10^{-1}	1.169×10^{0}	5.432×10^{-1}	8.472×10^{-3}	1.130×10^{-1}
469	1.251×10^{0}	5.236×10^{-1}	1.311×10^{0}	6.076×10^{-1}	9.489×10^{-3}	1.243×10^{-1}
470	1.408×10^{0}	5.883×10^{-1}	1.471×10^{0}	6.827×10^{-1}	1.083×10^{-2}	1.572×10^{-1}

$\alpha'_\ell(r_j)$ in Rydbergs

$r_j = \exp(-6.125 + j/64)$ a.u.

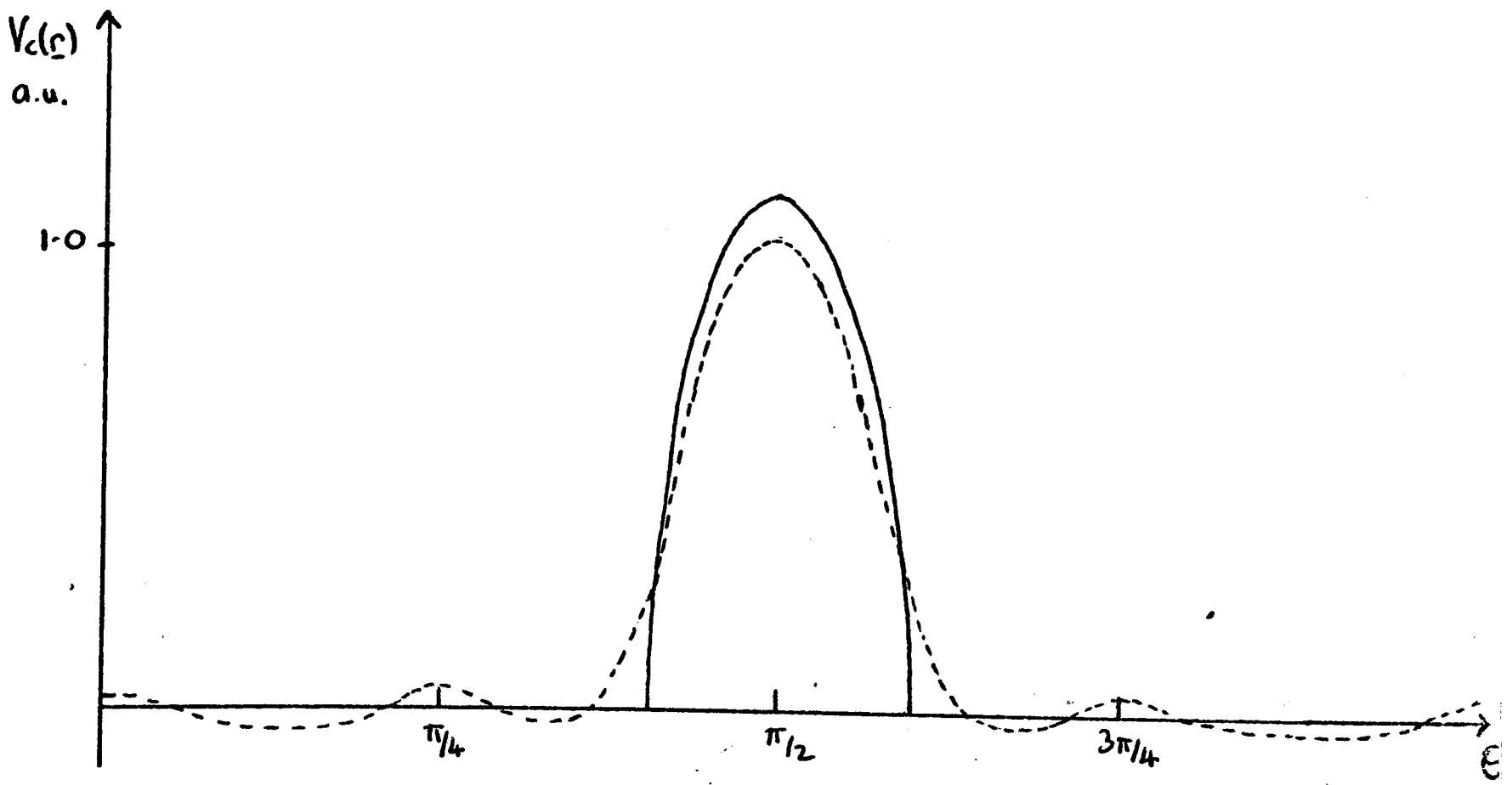
(Berglund and Spicer, 1964 a and b) and de Haas van Alphen periods (Koch, Stradling and Kip, 1964, and Joseph, Thorsen, Gertner and Valley, 1966). Improvements in this respect will only be expected when an improved basic potential field is developed. Such developments will include non-spherical corrections, perhaps similar to the ones obtained here, but in the case of copper at least, more important will be the removal of the Slater exchange approximation (Slater, 1951), replacing it by a treatment which considers electron correlation and screening in more detail, as for example done for the simple metals by R.C. Harford (1972), and the development of a self consistent approach which is clearly important in this transition series with its overlapping 3d and 4s bands. These changes are at present being explored by other members of the department, and their details will be presented, in due course, in other places. When all these considerations are incorporated, then we should expect to see an improvement in the band energy results as compared with experimental measurements. We can, therefore, in this work expect to do no more than show that the changes in band energies, due to this small correction to the Cellular Method considered here, are very small (smaller, indeed, than many of the non-spherical corrections quoted in the opening chapter for other substances).

Table 6.2.1. presents the Chodorow potential as employed by Burdick, whilst Table 6.2.2. gives the calculated expansion coefficients of the non-spherical correction to this potential due to the overlapping lentil-type regions discussed in Chapter 3 above. It is interesting to observe the relative sizes of these coefficients for different ℓ-values:- the $\ell = 6$ coefficients being generally almost three times the size of those for $\ell = 4$, and the $\ell = 10$ coefficients two orders of magnitude lower than those of $\ell = 6$. Taking these



Evaluation of equation (6.2.1.) for $r = r_c$, $\phi = 0$

Figure 6.2.1.



Evaluation of equation (6.2.1.) for $r = r_c$, $\phi = \pi/4$

Figure 6.2.2.

observations into consideration, it seems appropriate to curtail the expansion at $\ell = 8$ to give a reasonable approximation to the correction potential. In order to provide a good visual check, the expansion

$$V_c(\underline{r}) = \sum_{\ell=0}^{8} \alpha'_\ell(r)\, X_\ell^{\Gamma A_{1g}}(\hat{\underline{r}}) \qquad (6.2.1.)$$

was reconstructed, evaluated and plotted on graphs for

$$V(\underline{r}) , \quad \underline{r} = (r_c , \theta , 0) \qquad \theta = 0 \rightarrow \pi \qquad (6.2.2.)$$

and

$$V_c(\underline{r}) , \quad \underline{r} = (r_c , \theta , \pi/4) \qquad \theta = 0 \rightarrow \pi \qquad (6.2.3.)$$

These graphs appeared as shown in Figures 6.2.1. and 6.2.2., where the dotted curve represents the calculation from equation (6.2.1.), and the full lines the expected values, which can be seen to be appropriate from an examination of the position of the coordinate axes relative to the Wigner-Seitz cell (see Figure 3.4.2. of Chapter 3). The humps on these graphs appear at the positions of the corresponding overlap lentils. The expansion appears, from these graphs, to provide a fair representation of the true correction potential at the circumscribing sphere radius r_c.

6.3. The Coupling Coefficients.

Table 6.3.1. presents the coefficients calculated for coupling between the radial functions in the ΓE_g representation (chosen for convenience of size, having only nine harmonics up to $\ell = 12$, with respective ℓ-values of 2, 4, 6, 8, 8, 10, 10, 12, 12) at grid points spread over the region of overlap.

The values presented consist of only the lower triangle of each matrix, since it is easily deduced from the properties of these

Table 6.3.1.

The Coupling Coefficients $a_{LL'}(r_j)$ at Various Grid Points (in a.u.).

	1	2	3	4	5	6	7	8	9
1	-3.390×10^{-5}								
2	-1.210×10^{-4}	1.701×10^{-4}							
3	1.833×10^{-5}	-4.527×10^{-5}	-2.203×10^{-5}						
4	5.628×10^{-6}	-1.577×10^{-5}	4.370×10^{-5}	-1.282×10^{-5}					
5	1.386×10^{-4}	-1.606×10^{-4}	-4.807×10^{-5}	-1.278×10^{-5}	7.499×10^{-5}				
6	9.604×10^{-5}	3.910×10^{-6}	-3.395×10^{-5}	-4.851×10^{-5}	9.694×10^{-5}	7.429×10^{-6}			
7	1.672×10^{-5}	1.369×10^{-4}	-1.242×10^{-4}	-1.964×10^{-5}	-6.715×10^{-5}	2.485×10^{-6}	7.834×10^{-5}		
8	0	7.490×10^{-5}	-1.265×10^{-5}	1.771×10^{-6}	-5.374×10^{-5}	2.211×10^{-5}	1.121×10^{-4}	-3.415×10^{-5}	
9	0	4.104×10^{-5}	3.375×10^{-5}	-9.052×10^{-5}	-7.170×10^{-5}	-4.515×10^{-5}	-2.585×10^{-5}	4.688×10^{-5}	-4.012×10^{-6}

j=449

	1	2	3	4	5	6	7	8	9
1	-6.153×10^{-3}								
2	-1.943×10^{-2}	2.333×10^{-2}							
3	-1.519×10^{-3}	-9.521×10^{-3}	-5.232×10^{-3}						
4	-2.073×10^{-3}	-3.609×10^{-3}	3.999×10^{-3}	-3.245×10^{-3}					
5	1.925×10^{-2}	-2.245×10^{-2}	-6.644×10^{-3}	-1.985×10^{-3}	1.155×10^{-2}				
6	1.127×10^{-2}	-9.950×10^{-4}	-7.951×10^{-3}	-8.694×10^{-3}	1.434×10^{-2}	-1.022×10^{-3}			
7	1.962×10^{-3}	1.948×10^{-2}	-1.717×10^{-2}	-3.034×10^{-3}	-8.183×10^{-3}	4.010×10^{-4}	1.226×10^{-2}		
8	0	8.787×10^{-3}	-3.725×10^{-3}	-1.570×10^{-3}	-8.956×10^{-3}	-1.066×10^{-3}	1.635×10^{-2}	-6.096×10^{-3}	
9	0	4.815×10^{-3}	5.853×10^{-3}	-1.398×10^{-2}	-1.061×10^{-2}	-5.549×10^{-3}	-2.585×10^{-3}	5.914×10^{-3}	-9.756×10^{-4}

j=456

Table 6.3.1. (Cont'd)

	1	2	3	4	5	6	7	8	9
1	$-2.269\ 10^{-2}$								
2	$-6.601\ 10^{-2}$	$7.073\ 10^{-2}$							
3	$-1.425\ 10^{-2}$	$-3.656\ 10^{-2}$	$-2.126\ 10^{-2}$						
4	$-1.258\ 10^{-2}$	$-1.476\ 10^{-2}$	$7.272\ 10^{-3}$	$-1.328\ 10^{-2}$					
5	$5.898\ 10^{-2}$	$-6.932\ 10^{-2}$	$-1.992\ 10^{-2}$	$-6.979\ 10^{-3}$	$3.794\ 10^{-2}$				
6	$3.000\ 10^{-2}$	$-6.406\ 10^{-3}$	$-3.210\ 10^{-2}$	$-3.127\ 10^{-2}$	$4.600\ 10^{-2}$	$-8.070\ 10^{-3}$			
7	$5.223\ 10^{-3}$	$6.069\ 10^{-2}$	$-5.255\ 10^{-2}$	$-9.551\ 10^{-3}$	$-2.253\ 10^{-2}$	$1.035\ 10^{-3}$	$4.087\ 10^{-2}$		
8	0	$2.340\ 10^{-2}$	$-1.571\ 10^{-2}$	$-9.398\ 10^{-3}$	$-3.073\ 10^{-2}$	$-1.527\ 10^{-3}$	$5.196\ 10^{-2}$	$-2.181\ 10^{-2}$	
9	0	$1.282\ 10^{-2}$	$2.048\ 10^{-2}$	$-4.602\ 10^{-2}$	$-3.452\ 10^{-2}$	$-1.515\ 10^{-2}$	$-5.720\ 10^{-3}$	$1.644\ 10^{-2}$	$-4.175\ 10^{-3}$

j=463

	1	2	3	4	5	6	7	8	9
1	$-5.432\ 10^{-2}$								
2	$-1.531\ 10^{-1}$	$1.575\ 10^{-1}$							
3	$-3.967\ 10^{-2}$	$-8.749\ 10^{-2}$	$-5.190\ 10^{-2}$						
4	$-3.265\ 10^{-2}$	$-3.641\ 10^{-2}$	$1.210\ 10^{-2}$	$-3.228\ 10^{-2}$					
5	$1.318\ 10^{-1}$	$-1.556\ 10^{-1}$	$-4.379\ 10^{-2}$	$-1.678\ 10^{-2}$	$8.675\ 10^{-2}$				
6	$6.379\ 10^{-2}$	$-1.676\ 10^{-2}$	$-7.821\ 10^{-2}$	$-7.368\ 10^{-2}$	$1.045\ 10^{-1}$	$-2.217\ 10^{-2}$			
7	$1.111\ 10^{-2}$	$1.364\ 10^{-1}$	$-1.176\ 10^{-1}$	$-2.104\ 10^{-2}$	$-4.849\ 10^{-2}$	$1.794\ 10^{-3}$	$9.410\ 10^{-2}$		
8	0	$4.974\ 10^{-2}$	$-3.823\ 10^{-2}$	$-2.509\ 10^{-2}$	$-7.111\ 10^{-2}$	$-7.391\ 10^{-3}$	$1.177\ 10^{-1}$	$-5.125\ 10^{-2}$	
9	0	$2.726\ 10^{-2}$	$4.762\ 10^{-2}$	$-1.054\ 10^{-1}$	$-7.933\ 10^{-2}$	$-3.129\ 10^{-2}$	$-1.119\ 10^{-2}$	$3.509\ 10^{-2}$	$-1.052\ 10^{-2}$

j=470

coefficients, as discussed in Section 3.7. of Chapter 3, that

$$a^{j}_{LL'}(r) = a^{j}_{LL}(r) \qquad (6.3.1.)$$

It should also be pointed out that the diagonal terms do not, here, contain the contribution from the $\ell = 0$ correction term, since

$$\alpha_0(r) \int X^{j}_{L}(\hat{r})\, X^{\Gamma A_1 g}_{c}(\hat{r})\, X^{j}_{L'}(\hat{r})\, d\Omega = \frac{1}{\sqrt{4\pi}}\, \alpha_0(r)\, \delta_{L,L'} \quad , \qquad (6.3.2.)$$

where we have used the orthogonality properties of the symmetry adapted harmonics and the value of $X^{\Gamma A_1 g}_{o}(\hat{r})$ which is just $1/\sqrt{(4\pi)}$, and thus this term contributes only a constant value for all $L = L'$ which may just as well be added on to the spherical part of the potential.

It will be useful to make certain observations on the values in Table 6.3.1. :

(i) the coupling between both the 8th and 9th radial functions and 1st function is always zero. This is a direct consequence of the properties of the 3-j coefficients, since $\ell = 2$ can only couple with $\ell = 12$ through $\ell \geq 10$ (see equation (5.5.3.) of Chapter 5), whereas the maximum ℓ-value in the non-spherical potential expansion is $\ell = 8$, so that there can be no coupling in this case;

(ii) a comparison of the magnitude of these coefficients with the potential in the flat region around the muffin tin spheres (obtained from Table 6.2.1. as 4.695×10^{-1} a.u.) shows that the coefficients are not negligible in the outer regions of the cell, and therefore, if inaccurately calculated could lead to large shifts in the band energies obtained.

Having obtained these coefficients correctly, we can now move on to the band energy calculations which require the values of such coefficients.

6.4. The Band Energy Calculations.

Tables 6.4.1. to 6.4.7. give a complete presentation of the results obtained for the potential detailed above, calculated by the methods developed in Chapter 4. Also presented for comparison are the first order perturbation theory estimates of the non-spherically corrected eigenvalues, together with the set of results obtained by Burdick (1963) from the Chodorow potential.

We first deal with the convergence of the cellular expansion. Table 6.4.1. presents convergence tests on the original Cellular Method applied to the spherical potential for comparison with those given in Tables 6.4.2. to 6.4.4. for the new methods attempted. It is apparent that the convergence of the cellular expansion is less impressive for the second approximation treatment (Table 6.4.4.) than for the other two methods proposed. The ΓA_{1g} convergence is not quite so good for the non-spherical treatments as for the spherical case, but is still adequate, whilst for XE_g and LE_g the degree of convergence is seen to be comparable to that of the spherical case. Also notable is the agreement between the full and iterative non-spherical treatments for the different sizes of cellular expansion used. This supports the agreement between the methods apparent from Table 6.4.6., and discussed below.

Table 6.4.5. deals with the convergence of the iterative approximation to the non-spherical problem, showing two of the cases where the band energies differ most widely from those obtained from the spherical calculation. It is apparent from these that the method is converging for the problem considered, and that it should not be necessary to iterate more than four times on the cellular coefficients, and twice on each set of radial equations (see Section 4.6. of Chapter 4 for details of the method) in order to obtain suitable convergence.

Table 6.4.1.

Convergence of Cellular Expansion in Spherical Case

Rep \ ℓ-value	6	8	10	12
ΓA_{1g}	1.0413	1.0424	1.0424	1.0423
XE_g	0.5237	0.5247	0.5235	0.5236
LE_g	0.5369	0.5350	0.5354	0.5353

Table 6.4.2.

Convergence of Cellular Expansion for Full Non-spherical Treatment

Rep \ ℓ-value	6	8	10	12
ΓA_{1g}	1.0376	1.0408	1.0410	1.0412
XE_g	0.5237	0.5247	0.5235	0.5236
XA_{2u}	0.2389	0.2361	0.2371	0.2372
LE_g	0.5390	0.5358	0.5353	0.5355

Table 6.4.3.

Convergence of Cellular Expansion for Iterative Approximation

Rep \ ℓ-value	6	8	10	12
ΓA_{1g}	1.0355	1.0399	1.0401	1.0403
XE_g	0.5237	0.5247	0.5235	0.5236
XA_{2u}	0.2384	0.2363	0.2368	0.2369
LE_g	0.5390	0.5357	0.5353	0.5355

Table 6.4.4.

Convergence of Cellular Expansion for Second Approximation

Rep \ ℓ-value	6	8	10	12
ΓA_{1g}	1.0815	1.0655	1.0662	1.0666
XE_g	0.5234	0.5247	0.5234	0.5235
LE_g	0.5383	0.5362	0.5366	0.5369

Table 6.4.5.

Convergence of Iterative Approximation with Number of Iterations on Radial Solutions and Cellular Coefficients

Iterations on Radial Functions \ Iterations on Cellular Coeffs.	2	3	4
1	1.0384	1.0415	1.0388
2	1.0403	1.0403	1.0403
3	1.0403	1.0403	1.0403

ΓA_{1g}

$\ell_{max} = 12$

Iterations on Radial Functions \ Iterations on Cellular Coeffs.	2	3	4
1	0.2364	0.2369	0.2364
2	0.2364	0.2365	0.2369
3	0.2364	0.2368	0.2369

XA_{2u}

$\ell_{max} = 12$

N.B. (i) All results in Tables 6.4.1. to 6.4.5. are in negative Rydbergs.

(ii) All results calculated using 128 boundary points.

Having established the necessary convergence properties, we now turn to Table 6.4.6. which contains the full set of results obtained for each proposed method of calculation. We first compare the three methods adopted to deal with the non-spherical potential, using the full non-spherical treatment, which is the formal equivalent of the spherical Cellular Method with no approximation, as a basis.

Comparing first the results of the approximate treatment with these, it is apparent that, although the former still produce changes from the spherical case which are never more than 0.02 Rydbergs, the method does produce erratic results, and cannot be relied upon to give anything more than a crude estimate of the correction - the results are even more widely spaced from those of the full treatment than are the first order perturbation estimates. Adding this to the inferior convergence properties of the cellular expansion in this case, we must dismiss the method as a possible general method for non-spherical energy band calculations, and move on to consider the other methods proposed.

Taking now the iterative treatment, it is clear that the agreement in results between this and the full non-spherical treatment is much more impressive. All results agree to within ~ 0.0004 Rydbergs, except in the case of ΓA_{1g}. This result can probably be attributed to the fact that the ΓA_{1g} wave function is almost entirely the $\ell = 0$ state (see Table 4.6.1. of Chapter 4), so that the coupling term between higher ℓ-value radial functions and $\ell = 0$ functions becomes rather large, and these radial functions will be sensitive to small changes in the cellular coefficients (see equation (4.6.2.) for an appreciation of the effect of a very small cellular coefficient ($\ell \neq 0$) in the denominator of the coupling term). This problem reflects the completely different approach adopted in the iterative method, as no such problem can arise in the full treatment.

Table 6.4.6.

A Comparison of Band Energies Calculated by the Methods of Chapter 4 for the low lying Symmetry Points in Copper.

(in negative Rydbergs)

Calculation / Rep.	Burdick's Results	Our Spherical Case	Full Non-Spherical Treatment	Iterative Approximation**	Second Approximation	First Order Perturb'n Results
ΓA_{1g}	1.043	1.0423	1.0412	1.0403	1.0668	1.0451
ΓT_{2g}	0.640	0.6390	0.6390	0.6390	0.6392	0.6391
ΓE_{g}	0.582	0.5801	0.5801	0.5801	0.5817	0.5803
XA_{1g}	0.776	0.7747	0.7749	0.7749	0.7762	0.7750
XB_{2g}	0.739	0.7387	0.7393	0.7393	0.7393	0.7395
XB_{1g}	0.540	0.5381	0.5386	0.5386	0.5405	0.5387
XE_{g}	0.527	0.5236	0.5236	0.5236	0.5235	0.5236
XA_{2u}	0.234	0.2339	0.2372	0.2369	0.2401	0.2369
LA_{1g}	0.775	0.7734	0.7735	0.7734	0.7776	0.7743
LE_{g}	0.642	0.6427	0.6428	0.6428	0.6466	0.6429
LE_{g}	0.538	0.5353	0.5355	0.5355	0.5369	0.5355
LA_{2u}	0.429	0.4293	0.4371	0.4367	0.4447	0.4304

All these for $\ell_{max} = 12$, and 128 boundary points

** Results for number of iterations necessary to give satisfactory convergence.

Table 6.4.7.

Results of Table 6.4.6. Calculated in Rydbergs above ΓA_{1g} Energy.

Calculations / Rep.	Burdick's Results	Our Spherical Case	Full Non-Spherical Treatment	Iterative Approximation **	Second Approximation.	First Order Perturb'n Results
ΓA_{1g}	0	0	0	-0.0009*	0	0
ΓT_{2g}	0.403	0.4033	0.4022	0.4022	0.4276	0.4060
ΓE_g	0.461	0.4622	0.4611	0.4611	0.4851	0.4648
XA_{1g}	0.267	0.2676	0.2663	0.2663	0.2906	0.2701
XB_{2g}	0.304	0.3036	0.3019	0.3019	0.3275	0.3056
XB_{1g}	0.503	0.5042	0.5026	0.5026	0.5263	0.5064
XE_g	0.516	0.5187	0.5176	0.5176	0.5433	0.5215
XA_{2u}	0.809	0.8084	0.8040	0.8043	0.8267	0.8082
LA_{1g}	0.268	0.2689	0.2677	0.2678	0.2892	0.2708
LE_g	0.401	0.3996	0.3984	0.3984	0.4202	0.4022
LE_g	0.505	0.5070	0.5057	0.5057	0.5299	0.5096
LA_{2u}	0.614	0.6130	0.6041	0.6045	0.6221	0.6147

* these results use ΓA_{1g} from the full treatment as zero.

From the evidence presented in Table 4.6.4., and also the agreement in convergence data discussed above, it seems that the iterative method developed is wholly adequate in dealing with the problem encountered in this work, particularly if one adopts the procedure of always calculating ΓA_{1g} energies by the full treatment. The deviations from sphericity in this case are not really large enough for the results to justify the method conclusively, and further investigations will be necessary in a more representative case before the method can be relied upon generally. As pointed out in Chapter 4, the validity of the method is important, as it is very much quicker to compute than the full treatment, particularly as the size of the cellular expansion increases (see Table 6.4.8. for a series of comparisons).

A comparison with the first order perturbation results is very much as expected: the method always gives a reasonable estimate, though we cannot expect more than this when the expansion coefficients of the non-spherical potential are as large as those shown in Table 6.2.2. in comparison to the basic potential (Table 6.2.1.). This observation is in keeping with the work described in Chapter 1, where several workers (e.g. Kane, 1971) treat the "non-flat" potential exactly, only feeling perturbation theory to be justified within the inscribed sphere radius.

We now compare the results of the non-spherical treatment with those of the spherical case. It is apparent from the above tables that there are differences in the results of the two approaches, and that these differences, although small, are significant within the numerical accuracy of the program (the non-spherical program, when run with zero coupling coefficients, gave energy eigenvalues agreeing to four decimal places with those of the spherical program). The largest change in band energy produced by the non-spherical terms, for the representations calculated, is only 0.008 Rydbergs. It is not important for our purpose to decide which of the two sets of values is the best: the results show

that the non-spherical corrections, being of the order of a few milli-Rydbergs, cannot impair the theoretical significance of the agreement previously found between APW and spherical cellular caluulations (Altmann et al., 1968). The criticism levelled at the Cellular Method and discussed in Chapter 1 above, seems, therefore, to have little justification. This, as well as a numerical assessment of the present program, was the main purpose of this application of the non-spherical techniques developed during the course of this work.

Nevertheless, we shall discuss briefly the question of which set of results should be expected to be the more reliable - the spherical or non-spherical approach. There are two ways in which such a discussion may be conducted. The first, and most significant, would be to compare both sets of results with experiment, but as discussed in Section 6.2. above, such a comparison is worthless owing to the much greater uncertainty in the choice of potential. The other approach would be to analyse some simple model where the results of the spherical and non-spherical methods can be compared, which ought to give some feel for the relative accuracy of the two methods. Such an analysis is presented in the Appendix to this chapter.

In solving the Band Structure problem, we must deal with expansions of the wave functions in terms of a complete set. Although, for a spherically symmetric potential within the unit cell, it is natural to expand the wave functions in spherical harmonics, the eigenvalue problem would then no longer admit separable solutions since the boundary conditions on the eigenfunctions are prescribed on a non-spherical surface. The Cellular Method, therefore, chooses to handle the problem over the circumscribing sphere of the unit cell, where the spherical harmonics do provide a complete set in which to expand the wave functions. However, in

its exterior region, no sphere concentric with the cell is contained wholly within the cell, and the potential had to be doctored in this region in order to retain the sphericity of the problem. The present work has considered the truepotential within the whole circumscribing sphere, thus introducing non-spherical terms. The expansions of the wave functions over the circumscribing sphere of the cell are clearly different, depending on whether the true or doctored form of the potential is taken, and one would expect that the expansion obtained from the true potential would be the more reliable approximation over the circumscribing sphere.

Further, a well known theorem in the theory of generalised Fourier series (see, for example, Courant and Hilbert, 1953) states that among all possible linear combinations of a truncated complete set of orthogonal functions, the Fourier expansion yields the best approximation to the true function (in the root mean square sense), for the given truncation. It follows that the non-spherical based expansion used in the present work gives the better approximation to the exact solution within the circumscribing sphere, since this expansion is a generalised Fourier expansion derived from the true potential in that region.

The above discussion indicates that the non-spherical based expansion will give the better approximation to the true result over the circumscribing sphere of the unit cell. As pointed out, if the wave function over the whole cell (including its surface) is to

Table 6.4.8.

A Comparison of Computer Times for the Different Methods of Calculation with Various Expansion Sizes.

Method	Representation	No. of terms in Cellular expansion	Computer Time (secs.)
Spherical Case	ΓA_{1g}	5	38
-do-	XE_g	15	67
-do-	LE_g	22	110
Full non-spherical treatment	ΓA_{1g}	5	59
-do-	XE_g	15	393
-do-	LE_g	22	937
Iterative Treatment	ΓA_{1g}	5	54
-do-	XE_g	15	194
-do-	LE_g	22	388

All at $\ell_{max} = 10$

128 boundary points

Iterative treatment - { 3 iterations on cellular coefficients; 2 iterations on each set of radial functions.

be written as an expansion in spherical harmonics, then the expanion must be made over the circumscribing sphere. It should, therefore, be reasonable to suggest that the comparison over the circumscribing sphere will give a fair indication as to which is the better expansion. On this basis, we believe the non-spherical treatment to provide the better approximation to the true wave function over the unit cell, and thus the more reliable band energies.

6.5. Further Discussion on the Techniques Developed.

We showed in Chapter 1 that the radial Schrödinger equation is the basis of the APW and KKR methods, as well as of the Cellular Method, and its solution may be undertaken in the same way as described in Section 4.5. of Chapter 4 for all these methods. The properties of the coupling coefficients, as developed in Chapter 3 (or similarly developed for a different lattice structure) may still be used to simplify the problem, thus removing the need to search for a simplified form of APW expansion (as is done by Kleinman and Shurtleff, 1969) in order to overcome the computational difficulties involved in solving the coupled set of radial equations in that method. It is apparent from the work carried out here that the major increase in machine time in computing the full treatment of the non-spherical case will derive from the calculation of the more numerous radial functions. This will be the case whether the KKR, APW or cellular

Table 6.4.9.

A Comparison of various Transition Energies for Copper Based on Table of Connolly (1971) with Other Values Added.

Author	Method and Potential Used	$\Gamma T_{2g}-\Gamma A_{1g}$	$XA_{2u}-XE_g$	XE_g-XA_{1g}	$XA_{2u}-\Gamma A_{1g}$
Burdick (1963)	APW Chodorow	0.399	0.292	0.249	0.804
Butler (1969)	MOPW Chodorow	0.398	-	0.254	0.808
Arlinghaus (1965)	APW Chodorow	0.403	-	0.252	0.807
Altmann (1968)	Cellular Chodorow	0.403	0.289	0.251	0.808
Barton Present work	Cellular - non-spherical Chodorow	0.402	0.286	0.251	0.804
Wakoh (1965)	KKR Wakoh	0.388	-	0.242	-
Altmann (1968)	Cellular Wakoh	0.388	-	0.244	-
Snow (1968)	KKR - self-consistent 5/6 Slater exchange	0.375	0.317	0.224	0.794
Berglund et al. (1964)	Experiment Optical data	-	-	0.205	-
Cooper et al. (1965)	Experiment Optical data	-	0.331	-	-

approach is adopted. Thus the computing time will now almost certainly be shortest for the method which converges most quickly (note that the number of radial functions in the full treatment goes up as $(\ell_{max} + 1)^4$ for a general point in $\underline{k}$-space). Williams and Morgan (1974) in their tests on silicon in the work described in Chapter 1 above, claim that $\ell_{max} = 4$ gives results to within ~ 0.001 Rydbergs of the true result; from our results quoted above, it would seem that $\ell_{max} = 8$ would be required to secure such convergence in the Cellular Method. No direct evidence is available for the APW method in such calculations, although Kane (1971) requires $\ell_{max} = 9$ for his approximate approach to the non-spherical problem, also considered in Chapter 1. It therefore appears that the KKR method will suffer least from this large increase in number of radial functions, and in this respect will be the optimum method for such calculations. However, the simplicity of the Cellular Method, in its application to the non-spherical problem will prove attractive in many cases.

The iterative method developed in Section 4.6. of Chapter 4 also appears well suited to the APW method; all that is necessary is to consider, instead of the cellular expansion coefficients, the coefficients of the wave functions within the sphere, which are determined by matching to plane waves on the sphere in the standard way. However, the problem still remains with the APW method that the muffin tin sphere is essential to its operation, so that one cannot simply remove the spherical boundary condition when a non-spherical potential is considered. It does, therefore, appear that the APW method falls behind the KKR and Cellular Methods in this application.

In conclusion, it can be said that two methods of dealing with non-spherical potentials in the formulation of the Cellular Method have

been developed and tested here. The full non-spherical treatment will clearly be reliable in all cases, but involves a large increase in computing time from the spherical case. The iterative method works very well for the potential considered in this study, and requires much less computing time, but should be further tested in cases where the non-sphericity is of more significance. Such a case is that of graphite, where the high degree of non-sphericity of the Wigner-Seitz cell makes the muffin tin approximation a very poor one. Calculations of the band structure and Fermi surface, using the techniques developed here, are at present in progress in the department, and the results will, in due course, be presented elsewhere (C. P. Mallett - private communication).

Appendix.

Consider the two dimensional problem of a square lattice with lattice constant $\sqrt{2}$, as shown in the Figure B.1.

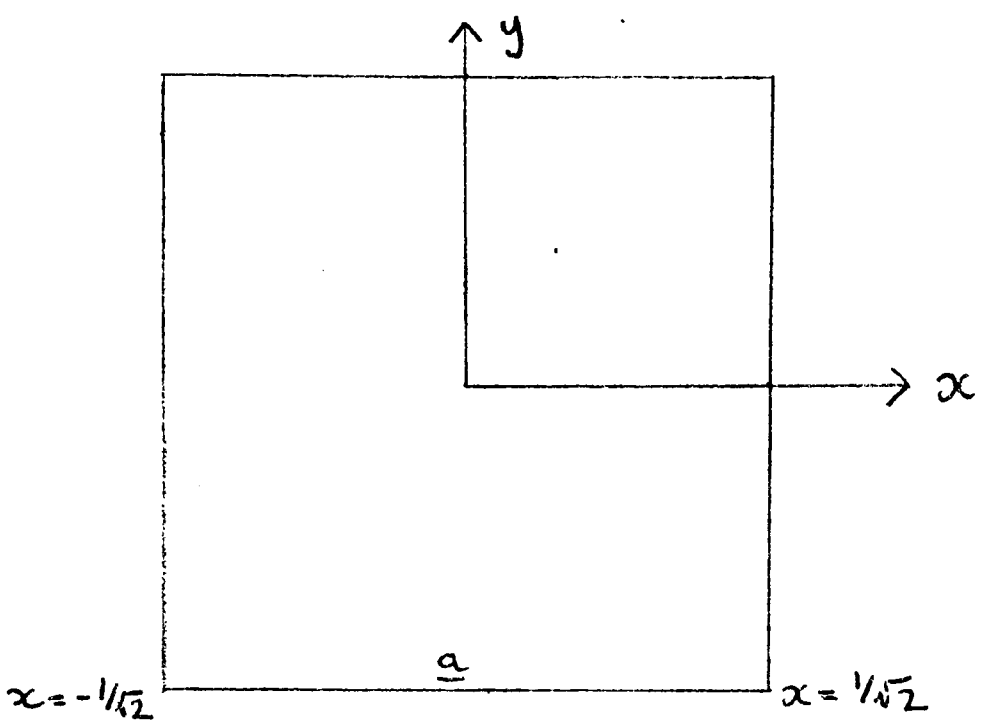


Figure B.1.

Take $\underline{k} = (\pi/\sqrt{2}, \pi/\sqrt{2})$, corresponding to a corner of the Brillouin Zone, so that $\underline{k} \cdot \underline{a} = \pi$. Take also a small representation symmetric under reflection on the two planes containing yz and xz . The Bloch boundary condition is then $\psi = 0$ on the cell boundary. Take the potential

$$V(x,y) = \tfrac{1}{2}(x^2 + y^2) \quad , \forall\ x,y \text{ in 1st unit cell}$$

$$= \text{periodic extension, outside 1st unit cell.}$$

The potential given is thus non-spherical.

We shall solve the problem in two ways. In the first we do not assume separability, i.e. we solve the problem precisely in the non-spherical approximation. In the second, the potential is doctored so as to be spherically symmetric within the circumscribing sphere of the unit cell, so that the Schrödinger equation can be separated. The Figures B.2 and B.3 below establish the notation to be employed.

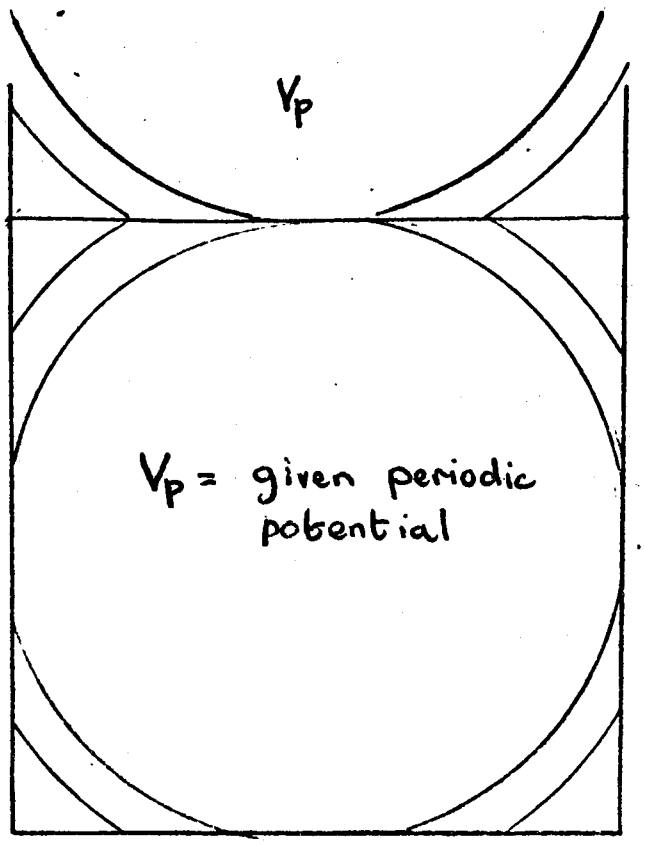


Figure B.2.

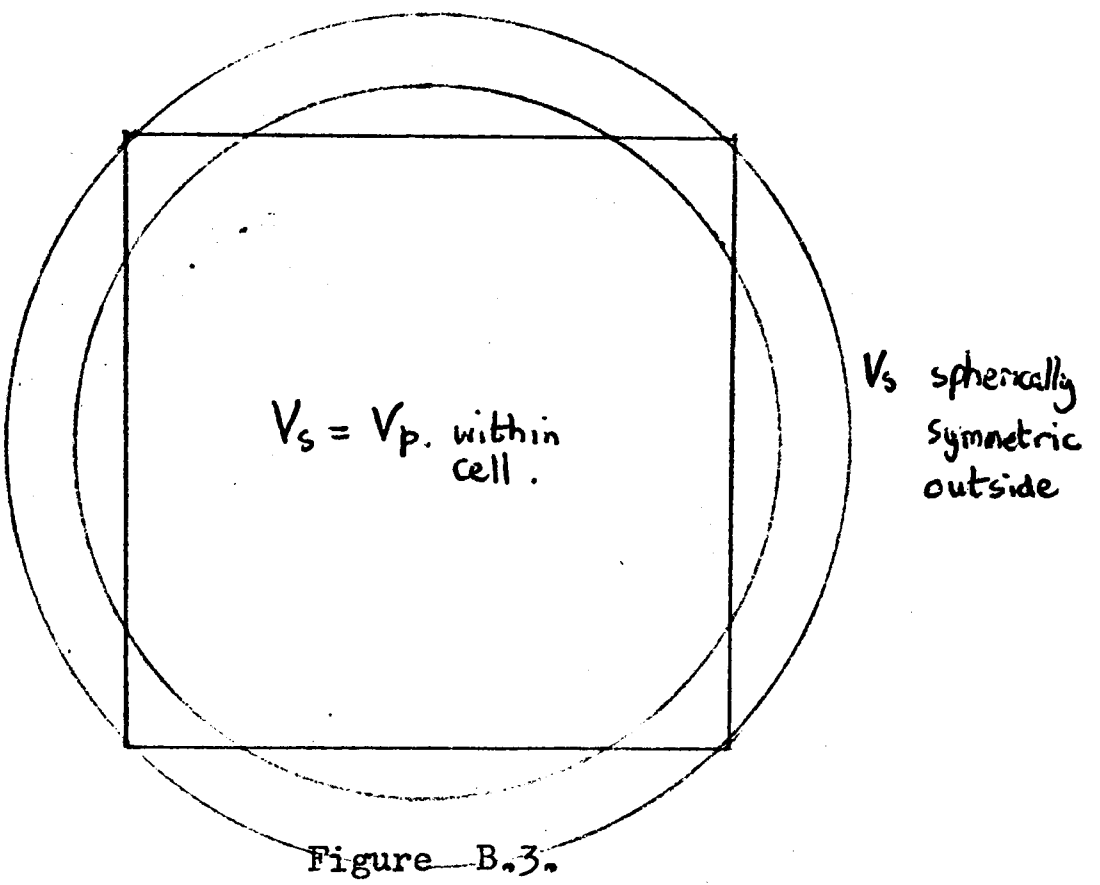


Figure B.3.

The Solution for V_p

We must solve the equation

$$-\tfrac{1}{2}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi_p(x,y)+\tfrac{1}{2}(x^2+y^2)\psi_p(x,y) = E\,\psi_p(x,y), \qquad \text{(B.1.)}$$

subject to the boundary conditions

$$\psi_p = 0 \quad \text{for} \quad x = \pm 1/\sqrt{2}\ , \ -1/\sqrt{2} \leq y \leq 1/\sqrt{2}, \qquad \text{(B.2.)}$$

$$\psi_p = 0 \quad \text{for} \quad -1/\sqrt{2} \leq x \leq 1/\sqrt{2}\ , \quad y = \pm 1/\sqrt{2}\ . \qquad \text{(B.3.)}$$

From the properties of the Hermite functions,

$$\psi_p(x,y) = 1/8\sqrt{\pi}\ H_2(x)H_2(y)\exp\left[-\tfrac{1}{2}(x^2+y^2)\right], \qquad \text{(B.4.)}$$

$$= 1/2\sqrt{\pi}\ (2x^2-1)(2y^2-1)\exp\left[-\tfrac{1}{2}(x^2+y^2)\right], \qquad \text{(B.5.)}$$

for the eigenvalue

$$E = 5\ . \qquad \text{(B.6.)}$$

The Solution for V_s

Writing (B.1.) in polar coordinates we obtain now for ψ_s ,

$$-\tfrac{1}{2}\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial^2}{\partial\phi^2}\right)\psi_s(r,\phi)+\tfrac{1}{2}r^2\psi_s(r,\phi)=E\psi_s(r,\phi). \qquad (B.7.)$$

Separating the variables by taking angular parts

$$\Phi(\phi) = \begin{cases}\cos m\phi \\ \sin m\phi\end{cases}, \qquad (B.8.)$$

we obtain the radial equation

$$\left(\frac{d^2}{dr^2}+\frac{1}{r}\frac{d}{dr}-\frac{m^2}{r^2}-r^2+2E\right)R(r)=0 . \qquad (B.9.)$$

In order to facilitate the solution of equation (B.9.) we write

$$R(r) = \exp\left(-\tfrac{1}{2}r^2\right)F(r), \qquad (B.10.)$$

which leads to the equation for f(r),

$$\frac{d^2F}{dr^2}+\left(\frac{1}{r}-2r\right)\frac{dF}{dr}+F\left(2E-2-\frac{m^2}{r^2}\right)=0 . \qquad (B.11.)$$

Take (as known from equation (B.6.) above) E = 5 in equation (B.11.) ,

so that

$$\frac{d^2F}{dr^2}+\left(\frac{1}{r}-2r\right)\frac{dF}{dr}+\left(8-\frac{m^2}{r^2}\right)f=0 . \qquad (B.12.)$$

This equation has two solutions :

$$m = 4 \quad \text{leading to} \quad f = r^4 , \qquad (B.13.)$$

and

$$m = 0 \quad \text{leading to} \quad f = \tfrac{1}{2}r^4 - 2r^2 + 1 . \qquad (B.14.)$$

Thus we obtain

$$\psi_s(r,\phi) = \left\{Ar^4\sin 4\phi + Br^4\cos 4\phi + C\left(\tfrac{1}{2}r^4-2r^2+1\right)\right\}e^{-\frac{1}{2}r^2} \qquad (B.15.)$$

On choosing A = 0 , and B, C suitably, we obtain

$$\psi_s(x,y) = \tfrac{1}{2}\sqrt{\pi}\,(2x^2-1)(2y^2-1)\exp\left[-\tfrac{1}{2}(x^2+y^2)\right] \qquad \text{(B.16.)}$$

satisfying $\psi_s = 0$ on the boundary.

Discussion.

It is apparent from the above analysis that the potential V_s

(i) gives the same eigenvalue as V_p

(ii) gives a wave function ψ_s which is equal to ψ_p inside the unit cell and on its surface. Also $\nabla_n \psi_s = \nabla_n \psi_p$ on the unit cell, since V_s is continuous with V_p at the surface of the cell.

Thus, if one can solve the Schrödinger equation exactly, the spherical method gives precisely the same results as the correct periodic potential. We shall now use the above analysis to illustrate a more general case.

ψ_s from equation (B.15.) and ψ_p from equation (B.4.) coincide only inside the unit cell. If ψ_s and ψ_p are expanded in a complete set of functions centred on the unit cell, the two expansions must be distinct although they will converge to the same value. Therefore, the truncated expansions for ψ_s and ψ_p must be different, and when these expansions are used to fit boundary conditions there is no reason for ψ_s to give the same result as ψ_p.

Since ψ_s and ψ_p differ outside the first unit cell, their truncated series also differ. It follows from the theory of the convergence of the Fourier series (see Section 6.4.) that the series for ψ_p gives the best approximation to the exact solution in the root mean square sense over the circumscribed sphere. We therefore expect that, on comparing the truncated expansions, that for ψ_p should give a better approximation than that for ψ_s over the unit cell.

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