THE D BAND IN COPPER

AND THE TRANSITION METALS

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ABSTRACT

The first part of the thesis deals with the tight-binding method of band structure calculation, particularly as applied to d bands, and the second part with the role of the d band in ferromagnetism.

A fundamental error in the tight-binding method arises from the use of a restricted set of trial functions. A method of calculating an upper bound to this error is given and an exact calculation of the error is made for a chain of δ-functions. The general conclusion is that the tight-binding method is only accurate when the nearest neighbour approximation is a good one. A method of calculating correction terms is given which is valid in cases of strong binding. The use of a 'muffin-tin' crystal potential is advocated. A criterion for choosing the 'atomic' functions is applied to the problem of calculating d bands. A correct choice ensures reasonable accuracy for states which do not interact with the sp band. A tight-binding calculation of the d band in copper is described; this employs a convenient method of reducing the energy integrals to the smallest number of independent ones and a new method of calculating three-centre integrals.

A band treatment of spin waves in metals is given. The thermodynamic properties of a ferromagnetic metal are discussed in terms

of spin wave excitations and independent particle excitations. Herring and Kittel's conjecture on the additivity of the two contributions to the specific heat, and to the deviation of the magnetization from saturation, is confirmed. The status of Stoner's collective electron theory is discussed. A formal proof is given of the existence of spin waves of long wavelength and a general method of calculating their energies, which depend strongly on the band structure, is outlined. Herring's and Izuyama's results on spin-wave energies are obtained as special cases.

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INTRODUCTION

CHAPTER 1

THE BASIS OF BAND THEORY AND ITS APPLICATION TO D ELECTRONS

The title of this thesis is the d band in copper and the transition metals, where the latter term is used with particular reference to those elements which appear just before copper in the periodic table and have incomplete 3d shells in the atom. This title presupposes that the behaviour of the d electrons in these metals may be described by band theory and it is one of the tasks of this introductory chapter to examine this assumption. Section 1 is a short introduction to one-electron band theory and section 2 deals with its basis in many-body theory. The concepts of many-body theory are important for the theory of ferromagnetism in the second part of the thesis. In section 3 some experimental data on d bands is reviewed and in section 4 an account of existing band structure calculations for copper and the transition metals is given.

1. One-electron theory

This section is concerned with the motion of a single electron in a potential field $V(\underline{r})$ which has the symmetry of a crystal lattice. The Schrödinger equation, in atomic units (i.e. the Bohr radius and the

Rydberg), is

$$H\psi = [-\nabla^2 + V(\underline{r})]\psi = E\psi \tag{1.1}$$

and this must be solved subject to certain boundary conditions which are indicated later. To classify the electronic states it is advantageous to use the methods of group theory. It is a well-known theorem that if a Hamiltonian is invariant under a group of operations, its eigenfunctions must form bases for the irreducible representations of the group. This leads to the prediction of degeneracies and of the way in which various eigenfunctions must transform under the operations of the group. The Hamiltonian in (1.1) is invariant under the operations which form the space group of the crystal. The space group consists of translation operators, the operators of the point group and possibly glide reflections and screw displacements. The point group consists of proper or improper rotations and reflections. Glide reflections and screw displacements are reflections or rotations, respectively, combined with a translation by a fraction of a basic lattice vector. A product of glide reflections and screw displacements can be a translation operator so when these elements are present the space group does not factorize into a translation group and a group consisting of the remaining operations. Glide reflections and screw displacements do not appear in cubic structures, with which this thesis

is mainly concerned, and since these operations complicate the group theory considerably they will not be considered further. When these operations do not occur the space group factorizes into the translation group and the point group; these may be considered successively.

1.1. Translational symmetry

A crystal may be divided into identical unit cells whose edges are represented by the vectors $\underline{a}_1$, $\underline{a}_2$, $\underline{a}_3$. If translation operators $T_{\underline{R}}$ are defined such that

$$T_{\underline{R}} \; V(\underline{r}) = V(\underline{r} + \underline{R}) \tag{1.2}$$

the translational symmetry of the crystal is expressed by the relation

$$T_{\underline{R}} \; V(\underline{r}) = V(\underline{r}) \tag{1.3}$$

where

$$\underline{R} = n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3 \tag{1.4}$$

and n_1, n_2, n_3 are integers. The operators $T_{\underline{R}}$ with $\underline{R}$ of the form (1.4) form a group which may be made finite by introducing periodic boundary conditions in the form

$$T_{\underline{R}+N\underline{a}_i} \equiv T_{\underline{R}} , \qquad i = 1, 2, 3.$$

The translation group consists of the N^3 operators $T_{\underline{R}}$ such that $\underline{R}$

is a lattice vector contained in the fundamental domain, which is a parallelepiped with edges $N\underline{a}_1$, $N\underline{a}_2$, $N\underline{a}_3$. Since this group is Abelian the irreducible representations are all one-dimensional. A wave-vector $\underline{k}$ is associated with each representation and the corresponding basis function is of the well-known Bloch form

$$\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot\underline{r}}\, u(\underline{r}) \tag{1.5}$$

where $u(\underline{r})$ has the periodicity of the lattice. The wave-vectors $\underline{k}$ are of the form

$$\underline{k} = (h_1\underline{b}_1 + h_2\underline{b}_2 + h_3\underline{b}_3)/N \tag{1.6}$$

where h_1, h_2, h_3 are integers and $\underline{b}_1$, $\underline{b}_2$, $\underline{b}_3$ are the basic vectors of a reciprocal lattice defined by

$$\underline{b}_i \cdot \underline{a}_j = 2\pi\delta_{ij} \tag{1.7}$$

The actual set of N^3 wave-vectors employed is arbitrary provided that no two wave-vectors in the set differ by a reciprocal lattice vector. The most convenient set to use are those wave-vectors contained in the unit polyhedron of the reciprocal lattice. This is the region of $\underline{k}$-space enclosed by planes which perpendicularly bisect the lines joining the origin to the nearest points of the reciprocal lattice; it is

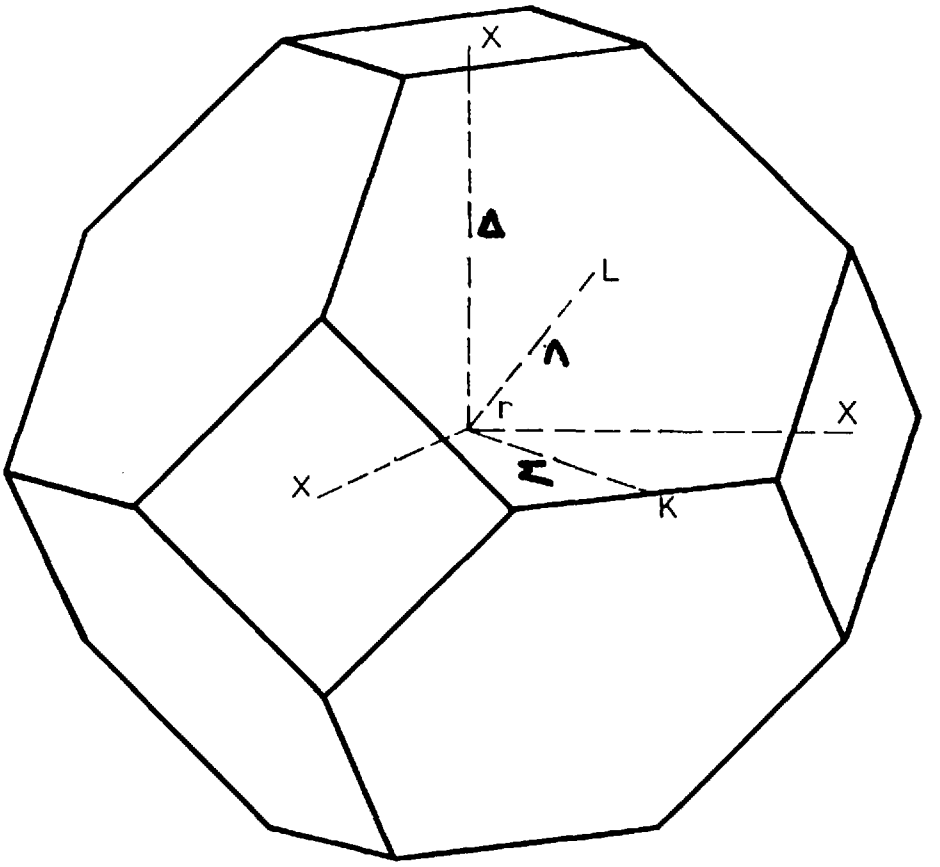

FIGURE 1: Brillouin zone for a face-centered cubic crystal, showing points and lines of high symmetry.

known as the Brillouin zone for the structure concerned. The Brillouin zone for the face-centred cubic lattice is shown in figure 1.

Since the eigenfunctions of (1.1) must form bases for the translation group, they are of the form (1.5). Hence the result of translational symmetry is that the electronic states in the crystal may be classified by wave-vectors $\underline{k}$ which lie within, or on the boundary of, the Brillouin zone.

1.2 Point group symmetry

A further classification of states with a given wave-vector $\underline{k}$ may be made using the symmetry properties associated with the point group. Suppose Q is an operator of the point group, then from (1.5)

$$Q\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k}\cdot Q\underline{r}}\, u(Q\underline{r}). \tag{1.8}$$

Now if the operation Q is applied in $\underline{k}$-space just as in real space one can write

$$Q\underline{k}\cdot Q\underline{r} = \underline{k}\cdot\underline{r},$$

or

$$\underline{k}\cdot Q\underline{r} = (Q^{-1}\underline{k})\cdot\underline{r},$$

and hence from (1.8)

$$Q\ \Psi_{\underline{k}}(\underline{r}) = e^{i(Q^{-1}\underline{k})\cdot\underline{r}}\ u(Q\underline{r}).$$

Thus, unless $Q^{-1}\underline{k}$ differs from $\underline{k}$ by a reciprocal lattice vector, the operator Q transforms $\Psi_{\underline{k}}$ into a function with a different wave-vector. Hence the only operators which are useful for classifying states of a given $\underline{k}$ are those which, when applied in $\underline{k}$-space, leave $\underline{k}$ unchanged or change it by a reciprocal lattice vector. These operators form a sub-group of the point group called the group of the wave-vector $\underline{k}$. The group of $\underline{k} = 0$ is the full point group. At a general point in the zone the group of the wave-vector consists only of the identity operator. Group theory is therefore much more powerful at points of high symmetry in the zone and this greatly facilitates the calculation of electron energies at these points. The points and lines of high symmetry are labelled by letters as shown in figure 1, where the notation of Bouckaert, Smoluchowski and Wigner (1936) is used. Representations of the groups associated with these points and lines are denoted by the corresponding letters with various suffixes and primes. Character tables and basis functions for the most important groups associated with many structures are to be found in the book by Jones (1960). Forms of character tables, for various sub-groups of the cubic group are given in tables 3 — 5 of this thesis; they are used there for a somewhat different purpose. The conclusion of the last two sections is that the eigenfunctions

of (1.1) are of the Bloch form (1.5), with wave-vectors k, and that they must form bases for the irreducible representations of the wave-vector groups.

1.3 Energy bands

The Schrödinger equation (1.1) has an infinite number of eigenfunctions belonging to each wave-vector $\underline{k}$ and to each representation of the wave-vector group. The energies corresponding to the eigenfunctions with wave-vector $\underline{k}$ may be enumerated in ascending order of magnitude as $E_1(\underline{k})$, $E_2(\underline{k})$ ... $E_n(\underline{k})$ ... The energy $E_n(\underline{k})$ varies continuously with $\underline{k}$ throughout the zone and its values form the n^{th} energy band. Examples of energy bands may be seen in figures 4, 17, 18 of this thesis. At points, or along lines, of symmetry in the zone the energies of two bands may coincide. These degeneracies are predictable since a n-fold degeneracy is associated with eigenfunctions which belong to a representation of the n^{th} order. Accidental degeneracies may also occur. Group theory is of great assistance in systematizing band theory and of practical value in calculation since at symmetry points in the zone one knows in advance the symmetries of the wave functions which are being sought. Nevertheless the practical problem of calculating energy bands is a difficult one and various methods for doing this are briefly discussed in section 4. The first part of the thesis is concerned particularly with one such method, the tight-binding method.

A spin-orbit interaction term has not been included in the Schrödinger equation (1.1). This is not to say that it is unimportant, since it plays an important role in some phenomena. However, our present knowledge of electronic states in many metals, particularly the transition metals, is still too inexact to justify the refinement of including spin-orbit interactions in our band-structure calculations. Nevertheless even for the transition metals the effect of spin-orbit coupling has been considered qualitatively (Lehman 1959, Callaway 1960). The situation may be contrasted with that for semiconductors such as germanium and silicon where the band structure is well-known and in which spin-orbit interaction plays a dominant role.

The one-electron energy band theory which has been sketched, together with the Pauli exclusion principle, forms the basis for a substantial part of the theory of metals. In the ground state of the metal the electrons occupy the states of lowest energy compatible with the Pauli principle i.e. such that no two electrons of the same spin occupy the same Bloch state. Thus, in a non-ferromagnetic metal at absolute zero, all Bloch states within a certain constant energy surface in $\underline{k}$-space are occupied by one electron of each spin, and all Bloch states outside that surface are unoccupied. The energy surface so defined is called the Fermi surface.

In an excited state of the system some Bloch states outside the

Fermi surface are occupied and some states within it are unoccupied. In other words there are some electrons outside the Fermi surface and some holes within it. In the simple independent electron theory the total energy of the system is taken as the sum of one-electron energies and the statistical mechanics of the system is simple. The probability of any given Bloch state being occupied at a given temperature is determined by the Fermi-Dirac statistics, and all the thermodynamic properties of the system are readily calculated. It is only necessary to know the density of states N(E), i.e. the number of Bloch states per unit range of energy.

This simple independent electron treatment is remarkably successful for describing properties such as electron specific heat and paramagnetic susceptibility of many metals. Band theory is also a moderately successful basis for discussing x-ray band widths. The reason for these successes has only been really understood in the last ten years and the simple band picture has been largely justified. The application of Fermi-Dirac statistics to electrons in metals was initiated by Sommerfeld (1928) and an extension to ferromagnetic metals was made by Stoner (1938, 1939). Stoner's theory has had impressive success in correlating data on ferromagnetic metals and alloys but has yet to receive an adequate justification. This problem is discussed in Chapter 6.

2. Band theory and the many-body problem

In the independent electron model no explicit account is taken of electron interaction. In fact the electrons interact strongly amongst themselves via Coulomb forces, and these interactions must be considered in a theoretical justification of the simple model. It has been mentioned that to a large extent such a justification has been achieved. However this thesis is mainly concerned with the transition metals and there still exists some doubt as to whether band theory can be applied to all the d electrons in some of these metals. In this section the methods which have been used to justify the band model are reviewed. In section 3 the evidence for the applicability of band theory to d electrons is considered.

In the independent electron model the potential V(r) in the Schrödinger equation may be assumed to take an averaged account of the charge distribution of the other electrons. This is the Hartree (1928) method and is equivalent to the use of a total wave function which is a single product of one-electron functions.

The Hartree-Fock method (Fock 1930) is to use a total wave function which is a determinant of one-electron functions; this has the anti-symmetry required by the Pauli principle. A set of coupled differential equations for the one-electron functions are obtained by a variational method and an important theorem due to Koopmans (1933) shows that certain Lagrangian parameters, which arise through a

normalization condition, may be interpreted as one-electron energies. However this apparent improvement on the Hartree theory leads to disaster. The density of states curve for free electrons, in which case the Hartree-Fock equations are easily solved, falls rapidly to zero at the Fermi surface and then rises again. This destroys all previous agreement with experimentally observed electronic specific heats. The trouble may be traced to certain exchange terms in the Hartree-Fock energy which arise through the determinantal form of the total wave function. It was pointed out by Wohlfarth (1950) that the trouble may be avoided by assuming a screened Coulomb interaction of the form $r^{-1} \quad e^{-\lambda r}$ ($\lambda \sim 10^{8} cm.^{-1}$) This assumption has since been justified by the work of Bohm and Pines (1953).

2.1 Bohm and Pine's theory

The difficulties of the Hartree-Fock theory are due to the neglect of correlation between electron positions. Wigner (1934, 1938) calculated the effect of this neglect on the ground state energy of the system but his method cannot deal with excited states. The first successful treatment of the correlation problem was that of Bohm and Pines (1953) for the free electron gas. An extension of the basic idea to real solids was first indicated by Mott (1954) and was subsequently worked out in detail by Nozières and Pines (1958).

The basic idea of the Bohm-Pines-Nozières (BPN) treatment is that a metal is in fact a plasma with an equal number of positively

charged ions and negatively charged electrons interacting via Coulomb forces. The plasma tends to remain in a neutral field-free state because of the screening action of the highly mobile electrons but there are oscillations about this equilibrium state. The Coulomb force may be divided into a short-range part and a long-range part, and the plasma oscillations arise from the long-range part. The method of BPN is to try to separate out the plasma motion, thus taking up the troublesome long-range part of the Coulomb force, and to leave the individual particles interacting via short range forces. To achieve this additional variables are introduced to describe plasma oscillations with all wave-vectors up to k_c, the maximum wave-vector for which a plasma oscillation exists as a fairly independent mode of excitation. For metals k_c^{-1} is of the order of the interelectron spacing. By adding suitable terms to the Hamiltonian for the system, together with certain subsidiary conditions on the wave function to compensate for this addition, and by making two canonical transformations, BPN are able to write the transformed Hamiltonian as the sum of two independent parts. The first part describes the plasma oscillations with frequencies given by a dispersion relation; the frequencies are usually not far removed from the classical free electron plasma frequency $\omega_p = (4\pi Ne^2/m)^{\frac{1}{2}}$ where N is the electron density. The second part describes a set of particles which interact only via short range forces, (the range is of order k_c^{-1}). Actually the particles also interact via a weak long-

range force and the particle wave function is subject to subsidiary conditions. BPN suggest that these complications may be neglected. It should be mentioned that the particles described by the transformed Hamiltonian are not the original electrons but rather, in the language of field theory, 'dressed' electrons. The separation into plasma oscillations and nearly independent particles can only be effected if two conditions are satisfied. These are expressed in terms of optical oscillator strengths for interband transitions which obey the sum rule. The first is an 'existence' criterion for plasma oscillations and demands that a sizeable fraction of the oscillator strengths must correspond to transitions of frequency well below ω_p. This is equivalent to demanding that the solid is moderately polarizable. The second condition is a 'convergence' criterion that the majority of oscillator strengths must correspond to frequencies much larger or smaller than ω_p. This is the condition that the plasma oscillations exist as fairly independent modes of excitation and do not decay too quickly into single particle excitations. The application of these criteria in the transition metals is discussed in section 3. A typical plasma excitation energy is of the order of 15 e.v. and plasma oscillations are not excited thermally. The result of the BPN treatment is that for most purposes a metal behaves as a system of almost independent particles described by a Hamiltonian

$$H = \sum_i \left[-\nabla_i^2 + V(\underline{r}_i) \right] + H_{s.r.} \quad . \qquad (1.9)$$

$H_{s.r.}$ represents the short-range interactions and the one-electron potential $V(\underline{r})$ is that arising from the ion cores screened by a uniform neutralising positive charge. Of course the problem of particles interacting via short range forces is still a complicated many-body problem and short range correlation effects may sometimes be very important (see section 21). However a reasonable approach to a band structure calculation is to attempt a Hartree-Fock treatment of the Hamiltonian (1.9) and this has been done by Heine (1957) in his calculation on aluminium. None of the previous difficulties arise from the exchange terms since the long-range part of the Coulomb force has been removed. No more than qualitative results can really be expected from the BHN approach since the approximations made are rather difficult to justify. If accurate a priori calculations of excitation energies in real solids are ever made, it seems more likely that it will be through the use of many-body perturbation theory and this method is discussed in the next section.

2.2. Many-body perturbation theory: quasi-particles

The method of many-body perturbation theory is a very direct one. The unperturbed system is taken to be that of the independent electron model, with Hamiltonian defined by the first term of (1.9), and the whole Coulomb interaction between electrons is treated as a perturbation. The second order terms in the Rayleigh-Schrödinger series diverge and one must sum to all orders to obtain a convergent result.

All the perturbation methods used to solve the many-body problem are essentially equivalent to the Rayleigh-Schrödinger series although the formulations appear rather different. A feature which all the methods have in common is that diagrams, similar to those used by Feynman ~~(1949)~~ in quantum field theory, are used to represent the different terms in the series. This facilitates the removal of divergencies. The different methods employed will now be mentioned briefly.

Goldstone (1957) and Hubbard (1957, 1958) have used a time-dependent adiabatic formulation in which the Coulomb interaction is imagined to be turned on slowly. They consider only the ground state of the system and Kohn and Luttinger (1960) and Luttinger and Ward (1960) have shown that this is given incorrectly if the Fermi surface is non-spherical. The error is due to the failure of the adiabatic approximation. The first treatment of excited states was given by Hugenholtz (1957), (1958) using a time-independent method and they are included in Luttinger's (1960) treatment of the thermodynamics of an interacting electron system.

The most important result of these various treatments is that the low-energy excited states of a metal may be described in terms of electron-like and hole-like excitations, where these 'quasi-particles' have a well-defined band structure $\epsilon(k)$ near a well-defined Fermi surface. It must be remembered that this conclusion is only valid

if the perturbation series converges and this should be investigated in principle in any particular case. The concept of a Fermi surface for a system of interacting particles and the concept of a quasi-particle must now be discussed. The subject has been reviewed by Falicov and Heine (1961).

The ground state wave function of a system of non-interacting particles is a single Slater determinant and the occupation number n_k of Bloch states is shown in figure 2(a). Here n_k is plotted against k for an arbitrary direction in $\underline{k}$-space and k_F is the point of intersection with the Fermi surface. The latter is clearly defined by the discontinuity in n_k. In an interacting system, where the ground state wave function is a sum of many Slater determinants, one might expect that the mean occupation number $\overline{n}_k$ would vary as shown in figure 2(b) and that no well-defined Fermi surface would exist. However it was suggested by Migdal (1957), and proved to be the case if perturbation theory is valid by Luttinger (1960), that a discontinuity in $\overline{n}_k$ persists as shown in figure 2(c). A perturbed Fermi surface is therefore defined and is found to have the same volume as that of the interaction-free system. Luttinger further showed that, at low temperatures, equilibrium properties such as electronic specific heat are given by formulae identical with those of the independent electron model except that the original one-electron energies are replaced by certain quasi-particle energies. These quasi-particle energies, or

"true" single-particle excitation energies as Luttinger calls them, are given as solutions of well-defined equations. The "true" band structure of a solid, which if used in the normal formulae would lead to correct low-temperature equilibrium properties, should thus be determined by solving these equations, but this does not appear feasible at present. A treatment of a non-equilibrium property, electrical resistivity, has been given in terms of quasi-particles by Langer (1961).

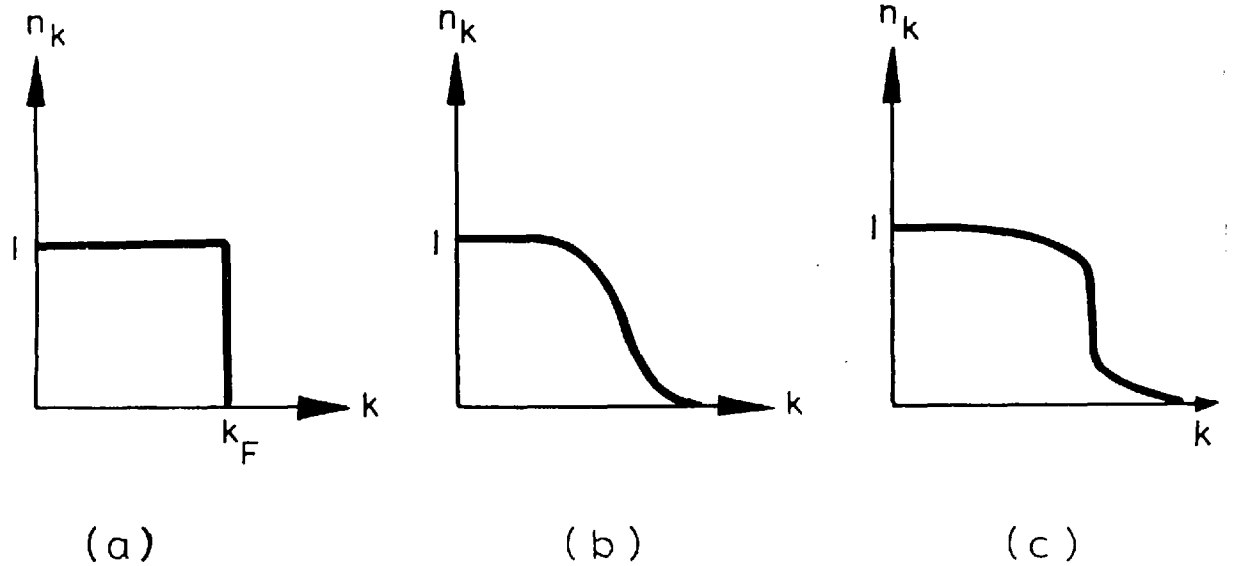

Fig. 2

The results of the work described above imply that the excitation energies of the low-lying states of a many-electron system may be written as a sum of independent quasi-particle energies. The picture of a quasi-particle is as follows. A quasi-particle differs from an actual electron or hole in that it is not a point particle but includes all the local disturbance in the electron gas which screens the charge.

Thus quasi-particles interact via short range screened Coulomb forces. Since the density of quasi-particles is low at normal temperatures, this interaction may usually be neglected. Even a state in which a single quasi-particle $\underline{k}$ is excited is not an exact eigenstate of the system and decays with a lifetime $\tau(\underline{k})$ into more complicated states. However $\tau(\underline{k})$ is proportional to $[\epsilon(\underline{k})-\epsilon_F]^{-2}$ so that the lifetime tends to infinity at the Fermi level. The finite lifetime of a quasi-particle can usually be neglected since the excitations normally produced have a sufficiently low energy that their lifetime is much longer than the relaxation time due to scattering by lattice vibrations and impurities.

It has been seen that as long as the series converges, many-body perturbation theory justifies a band picture based on an independent quasi-particle model. The practical problem of calculating quasi-particle band structures presents enormous difficulties but attempts to formulate the problem in a reasonable way have been made by Pratt (1960) and Phillips (1961).

The limitations of perturbation theory must be mentioned. The states discussed in this section are all of the type described as 'band-type' in Chapter 6; they have a direct correspondence with a single determinant state of the interaction-free system. There are other types of states, such as the spin wave states of Chapter 6, that do not have this correspondence and are not obtained by normal perturbation theory. The second point to emphasize is that a Fermi surface

has only been shown to exist if the series converges. This is not always the case, for example in the ground state of superconductors or in a system of well-separated hydrogen atoms. In the latter case, in the limit of infinite separation, $n_k = \frac{1}{2}$ throughout the Brillouin zone. Whether the Fermi surface disappears gradually or abruptly with increasing separation is an interesting question discussed by Mott (1961).

3. d electrons in the transition metals

The object of this section is to discuss the applicability of band-theory to d electrons in the transition metals and to indicate some experimental work which throws light on the band structure. Nearly all properties of the transition metals depend directly or indirectly on this band structure and no complete review can be given here. The theory of these metals is not yet in a state where very detailed comparison with experiment can be made. The basic picture of the band structure of copper and the transition metals is due to Mott (1935). It consists of a rather narrow 3d band, with a high density of states, which is overlapped by a broad sp band with low density of states. In copper the d band is full but in the transition metals there are holes in the d band. Of course mixing occurs between states of d, s and p symmetry but the onset of the 'd' band as one approaches from higher energies is quite clearly defined by a sharp rise in the density of states. A division of the states into a 'd'

band and a 'sp' band is very convenient, particularly in the theory of ferromagnetism where one deals with holes in the d band. This division is not really objectionable. The assumption often made of a fixed number of holes in the d band corresponds to a clear-cut approximation; one selects in a fairly natural way a set of states to form a d band and then neglects possible transitions of electrons from other states (the sp band) into the selected ones. This approximation is probably quite a good one since the density of states of the sp band is low.

It is natural to enquire whether the theoretical work described in section 2 can provide a justification for the use of straight-forward band theory in the case of d electrons. Unfortunately no definte decision can be made on the basis of either plasma theory or many-body perturbation theory. In the latter case it is impossible to examine the convergence of the series involved. In the case of plasma theory it is found that although the 'existence' criterion discussed in section 2 is satisfied, the 'convergence' criterion is not. Optical measurements (Ehrenreich and Philipp 1962) on copper show that oscillator strengths involving d and/or s electrons are distributed over a wide frequency range which includes plasma frequencies calculated for the s electrons alone and for the s and d electrons together. No separation of the plasma is really possible and no justification is given for a simple picture of all the s and d electrons interacting only via short-range forces. It cannot be deduced that band theory applies to

all the d electrons.

The experimental evidence for the applicability of band theory is also ambiguous in some cases. However in nickel and cobalt it is almost certain that the d electrons must be described by band theory. The ferromagnetism of these metals is due to the d electrons, and their non-integral magneton numbers, 0.6 for Ni and 1.7 for Co, are difficult to explain on a localized model. Mott and Stevens (1957) have assembled considerable experimental evidence for their theory that in iron the two magnetic electrons are localized. The magneton number of iron is 2.2 and the additional 0.2 spins per atom are attributed to polarization of the spins of the other electrons. Much of the experimental evidence, however, can be interpreted on the basis of band theory if suitable assumptions about the band structure are made. A strong piece of evidence in favour of a localized model for iron was provided by the x-ray determinations of electron density made by Weiss and De Marco (1958). They found that the electron density in iron differed markedly from that in copper, nickel and cobalt and corresponded to only two electrons in the rather compact d orbitals. Mott and Stevens suggested that those two electrons were the localized magnetic ones and that the other electrons were in rather diffuse states formed from s, p and d functions. This picture was criticized on purely electrostatic grounds (see e.g. Herring 1960) and the x-ray evidence has since been revised. Batterman, Chipman and De Marco (1961) find that in fact the d electron distribution is not much different from

that in the free atom. Nevertheless the uncertainties seem to be such that it is difficult to reject Mott and Stevens' model categorically.

Herring (1960) has stressed the need for experimental investigations of the Fermi surface in transition metals. Methods such as cyclotron resonance and anomalous skin effect which have been found useful in other metals have not yet been applied to the transition metals. The necessary condition for success is $\omega_c \tau > 1$, where ω_c is the cyclotron frequency ($eH/m^* c$) of carriers of effective mass m^* in the magnetic field H and τ is the carrier relaxation time. This condition is difficult to achieve, particularly for the heavy d electrons. The first direct information about the Fermi surface of a transition metal has recently been obtained by Fawcett and Reed (1962) who observed the anisotropy of the high-field magnetoresistance of a nickel single crystal. However they apparently only achieve a condition $\omega_c \tau \sim 1$ for the sp electrons and their data is consistent with a surface having the topology of the copper Fermi surface (Pippard 1957). Detailed experimental information on the d electron part of the Fermi surface is going to be very difficult to obtain. However information on the density of states at the Fermi surface is readily obtained from electronic specific heat measurements and the high values observed in the iron group of metals are consistent with a high density of states in the d band. The

structure of the d band is all-important for the ferromagnetism of the transition metals and this is discussed fully in part 2 of this thesis.

Electron transport properties depend on the band structure and the scattering probabilities. In the transition metals the current is mainly carried by the s electrons but Mott (1935) pointed out that the scattering probability is roughly proportional to the large density of states in the d band at the Fermi surface. This observation leads to a satisfactory qualitative theory of the observed resistivity anomaly at the Curie point and of the large negative thermoelectric power for nickel. The complicated galvanomagnetic properties of ferromagnetic metals appear to depend strongly on the 3d states in the presence of spin-orbit interaction. The tight-binding approximation has been used to discuss this type of problem (Berger 1963). Another phenomenon involving spin-orbit interaction is that of ferromagnetic anisotropy. Fletcher (1954) was able to use the results of his earlier tight-binding calculation (Fletcher 1952) to calculate the anisotropy coefficient in nickel. A corrected value (Fletcher 1961) is not in bad agreement with experiment. The comparative simplicity of the tight-binding method makes it very useful for detailed calculations of this sort.

X-ray emission spectra should provide information on the density of states in the d band but the interpretation of the results is difficult (see e.g. Skinner, Dullon and Johnston 1954). The observed band

widths of several e.v. in the transition metals agree roughly with theoretical estimates. Optical reflectance data on semiconductors has recently provided considerable information about their band structures over quite a wide energy range (Ehrenreich, Philipp and Phillips (1962)). Ehrenreich and Philipp (1962) have applied similar methods to copper and are able to identify a number of interband transitions on the basis of Segall's (1962) calculated band structure.

Perhaps the most fundamental property of a solid is its cohesion. It is generally believed that the d electrons in the transition metals contribute a large part of the binding energy. A detailed calculation for iron by Stern (1959) using a tight-binding method gives good agreement with the observed value.

4. Methods of calculating the structure of d bands

It is clear that much theoretical and experimental work remains to be done before detailed comparisons can be made between calculated band structures and experimental data. Work on the purely mathematical problem of solving the one-electron Schrödinger equation for an assumed periodic potential is only just reaching the stage where reliance can be placed on the results. However a situation has now been reached where calculations by different methods, but using the same potential, yield identical results. This has been shown explicitly

by the work of Segall (1962) and Burdick (1963) on copper. It also appears that band structures may not be as sensitive to the exact potential used as has sometimes been thought. Some discrepancies between calculations seem to have been due to inadequate solutions of the periodic potential problem itself. In the case of the transition metals it seems that the structure of the s and d bands themselves may be relatively insensitive to the exact potential used but that their position relative to each other is quite sensitive to this potential (see Manus 1960-62).

The first part of this thesis is devoted to the tight-binding method of band structure calculation which has proved one of the most useful methods for d bands. In this section a brief review is given of other methods and their application to d bands. Only fairly recent applications are mentioned since these are probably the most accurate; references to earlier work can be found in the review by Callaway (1958).

Methods of band structure calculation fall into two catergories. First, those in which the wave functions satisfy the boundary conditions (i.e. the Bloch condition) exactly but the Schrödinger equation only approximately and, secondly those in which the Schrödinger equation is satisfied exactly but the boundary conditions only approximately. In the first type of calculation the wave function is expanded in a set of Bloch functions and the variational method leads to a secular equation for the energies. It is necessary to choose the expansion set in such a

way that convergence is rapid, so that only secular equations of reasonable size need be solved. At symmetry points in the zone the order of the secular equation is reduced, since for a given energy level only trial functions of a predetermined symmetry need be considered. Examples of this type of calculation are the orthogonalized plane wave (OPW) method, the tight-binding method and the augmented plane wave (APW) method. The latter method is something of a hybrid since trial functions are constructed by solving the Schrödinger equation exactly within a sphere inscribed in the unit cell and joining this continuously onto a plane wave in the outer part of the cell. This method leads to rapid convergence in many cases and may be used at general points in the zone. Methods of the second type are the cellular method and the Green's function method. Once again group theory is useful at symmetry points in the zone and the cellular method can be very good at such points. However, the difficulties of satisfying the boundary conditions on the cell boundary make the method unreliable at a general point in the zone. The Green's function method (Kohn and Rostocker 1954, Ham and Segall 1961) is much superior in this respect. The method is initially restricted to a 'muffin-tin' form of potential (one in which the potential is constant between inscribed spheres) but deviations of the potential from this form may be treated by perturbation theory. Various calculations on different metals will now be mentioned.

Callaway (1955) used the OPW method in a calculation on the d band in body-centred iron. He found that even at the symmetry points to which his calculation was restricted, reasonable convergence could only be achieved by supplementing the OPW set of functions with functions of d symmetry localized on atoms. Callaway used a potential corresponding to the configuration in the free atom and this led to a narrow band width of rather less than 2 e.v. Because of poor convergence the OPW method is not well adapted to d band calculations.

Howarth (1953) used the cellular method for copper and later used the APW method (Howarth 1955) for a potential which was identical with the cellular one within the sphere inscribed in the unit cell. He obtained very different results for the d band in the two calculations and this was attributed to extreme sensitivity to the detail of the potential in the outer region of the cell. It has since been suggested (Howarth, private communication) that the discrepancy is due to a faulty application of the APW method.

Hamus (1962), Wood (1962) and Burdick (1963) have used the APW method in calculations on nickel, iron and copper respectively. Quite good convergence is obtained at general points in the zone and Burdick's results coincide with those of Segall (1962) who used the Green's function method with the same potential. This latter method also converged quite rapidly. The copper Fermi surface deduced from the calculations of Segall and Burdick is in agreement with the Pippard (1957)

model deduced from experiment.

The most accurate methods at present available for calculating d bands are the APW method and the Green's function method. Neither of these methods has the simplicity of the tight-binding method and it is the object of the first part of this thesis to examine whether the latter method can achieve reasonable accuracy.

PART 1

THE TIGHT-BINDING APPROXIMATION AND ITS USE FOR CALCULATING THE STRUCTURE OF D BANDS

CHAPTER 2

INTRODUCTION TO THE TIGHT-BINDING METHOD

It was pointed out in section 3 that many properties of the transition metals depend on the behaviour of electrons in the 3d band. In particular a knowledge of this behaviour is essential to an understanding of the phenomenon of ferromagnetism which is the subject of the second part of this thesis. To achieve a detailed understanding of these properties it is necessary to know electron energies and wave functions at many points in the Brillouin zone. Unfortunately most methods of band structure calculation are restricted in practice to symmetry points in the zone and it is not possible to calculate the density of states, which is a vital piece of information. However density of states curves for 3d bands have been calculated by the tight-binding method (Fletcher, 1952, Belding 1959, Asdente and Friedel 1961) and the tight-binding interpolation method (Slater and Koster 1954, Wohlfarth and Cornwell 1961). The only calculations by other methods are those of Slater (1936), based on Krutter's (1935) calculation by the old cellular method, which is known to be inaccurate, and the recent APW calculations by Burdick (1963) and Wood (1962). This last calculation involved huge computational effort and yet, as Wohlfarth and Cornwell (1961) point out, Wood was still unable to cover a

sufficient number of points in the zone to give a fully reliable density of states curve. The most detailed curve yet obtained is that of Wohlfarth and Cornwell (1961) who fitted the tight-binding interpolation method to Wood's results. As well as its usefulness for calculating density of states curves, the tight-binding method has the advantage that the wave functions are simple enough to form a basis for physical theories.

It is clear from the above account that the tight-binding method occupies an important position in the theory of the transition metals. Unfortunately, however, although the utility of the method has been proved, its accuracy is largely unknown. Furthermore the tight-binding interpolation method can really only be regarded as reliable in situations where a rigorously applied a priori tight-binding calculation would also be accurate. It is, therefore, of importance to assess the accuracy of the tight-binding method for calculating the structure of d bands and this part of the thesis is concerned with this problem. However, the work of Chapter 3 is quite general and not tied to the d band problem.

The first work the author did on this problem was an elaborate tight-binding calculation for the d band in copper using a crystal potential for which it was claimed (Howarth 1954) that accurate energies were known at symmetry points in the Brillouin zone. The aim of the calculation was to compare energies calculated by the

tight-binding method with the accurate ones. Although this very laborious calculation has some positive aspects the final result is the rather negative one that in this case the tight-binding method, as used there, is very inaccurate. For this reason a summary of this work has been relegated to Chapter 5 at the end of this part of the thesis. The lack of success in this initial calculation stimulated a general investigation of the basis of the tight-binding approximation and this is reported in Chapter 3. Methods are developed for calculating an upper bound to the error in a tight-binding calculation and for calculating corrections where necessary. These ideas are applied to d bands in Chapter 4 and the conclusions reached are summarized in section 13. This chapter is devoted to a general formulation of the tight-binding method and a survey of existing calculations.

5. Formulation of the tight-binding method

It is the purpose of this section to formulate the tight-binding method or method of linear combination of atomic orbitals (LCAO method) in a fairly general manner. The method as used in practice is an approximate one, but it may be considered as the first approximation in a potentially exact method. The nature of the approximation is then clear.

The tight-binding method is most appropriately used for the calculation of the structure of bands in which the electrons are fairly tightly bound, i.e. bands which may be considered as arising principally from a single atomic orbital or group of degenerate atomic orbitals. Suppose the periodic crystal potential to be used in the band calculation is

$$V(\underline{r}) = \sum_i v(\underline{r} - \underline{R}_i) \qquad (2.1)$$

where $v(\underline{r} - \underline{R}_i)$ is assumed to be spherically symmetric about the lattice point $\underline{R}_i$. The tight-binding method is particularly simple to formulate and to apply when $V(\underline{r})$ takes the 'muffin-tin' form used in the APW and Green's function methods of calculating band structures. In this case $v(r)$ is assumed to be zero outside a sphere of radius equal to or less than half the nearest neighbour distance. In the more usual case the radius is equal to this distance so that the sphere is inscribed in the unit cell and spheres about adjacent sites touch. This potential is referred to as a 'muffin-tin' potential with touching spheres, or frequently just as a 'muffin-tin' potential. The discussion will be restricted to this type of potential for the moment but more general potentials are discussed in section 6.5. For this type of potential thecrystal potential is just $v(r)$ within the region occupied by the ion core surrounding the origin and the core wavefunctions $u_1(\underline{r}) \ldots u_l(\underline{r})$ are solutions of the Schrödinger equation

$$\left[-\nabla^2 + v(\underline{r})\right] u_n(\underline{r}) = \epsilon_n u_n(\underline{r}) \tag{2.2}$$

subject to the boundary condition $u_n \to 0$ at infinity. The orthonormalized crystal core functions are

$$\chi_m(\underline{k},\underline{r}) = N^{-1} \sum_j e^{i\underline{k}\cdot\underline{R}_j} u_m(\underline{r}-\underline{R}_j) \tag{2.3}$$

as long as the overlap of core functions on neighbouring atoms may be neglected. The summation is over all N lattice sites $\underline{R}_j$ in the fundamental domain. The functions (2.3) are virtual ion core functions; they do not correspond to the real ion core states since they are calculated in the crystal field appropriate to the band whose structure is required and not in the Hartree-Fock field appropriate to the particular ion-core state. The functions (2.3) are solutions of the Schrödinger equation

$$H\psi(\underline{k},\underline{r}) \equiv \left[-\nabla^2 + V(\underline{r})\right] \psi(\underline{k},\underline{r}) = E(\underline{k})\,\psi(\underline{k},\underline{r}) \tag{2.4}$$

subject to periodic boundary conditions and correspond to the lowest eigenvalues $\epsilon_1, \epsilon_2 \ldots \epsilon_N$.

Suppose the complete set of eigenvalues of (2.4) is

$$\epsilon_1, \epsilon_2, \ldots \epsilon_\ell, E_1(\underline{k}), E_2(\underline{k}) \ldots E_n(\underline{k}) \ldots \quad . \tag{2.5}$$

The LCAO method for finding the eigenvalues $E_1(\underline{k})$, $E_2(\underline{k})$... is to attempt to expand $\psi(\underline{k},\underline{r})$ in terms of the Bloch functions

$$b_s(\underline{k},\underline{r}) = N^{-\frac{1}{2}} \sum_j \exp(i\underline{k}\cdot\underline{R}_j)\, g_s(\underline{r} - \underline{R}_j) \tag{2.6}$$

where the g_s are atomic-like wave functions. The $g_s(\underline{r})$ are taken as the complete set of normalised atomic-like orbitals satisfying a Schrödinger equation

$$[-\nabla^2 + U(r)]\, g_s = \xi_s g_s \tag{2.7}$$

subject to the boundary condition $g_s = 0$ on the boundary of the fundamental domain. The Bloch functions (2.6) are not in general orthogonal or normalised owing to the non-orthogonality of g_s orbitals on different lattice sites. The choice of the 'atomic potential' $U(r)$ is discussed below. The eigenvalues ξ_s form a discrete-continuous energy spectrum.

It is usually convenient to choose the spherically symmetric potential $U(r)$ as equal to $v(r)$ within the region occupied by the

ion core surrounding the origin but the form of $U(r)$ at larger distances from the origin need not be the same as $v(r)$. Thus the lowest eigenvalues of (2.7) are $\epsilon_1, \epsilon_2 \ldots \epsilon_\ell$ with corresponding eigenfunctions $u_1, u_2 \ldots u_\ell$. Hence $g_s \equiv u_s$, $s = 1, \ldots l$. Suppose the next lowest eigenvalue of (2.7) is E_0 with corresponding degenerate eigenfunctions $\phi_1, \ldots \phi_n$. The complete set of eigenvalues ξ_s and eigenfunctions g_s of (2.7) is then

$$\epsilon_1 \ldots \epsilon_\ell, E_0 \ldots E_0, \xi_{\ell+n+1}, \xi_{\ell+n+2}, \ldots$$
$$u_1 \ldots u_\ell, \phi_1, \ldots \phi_n, g_{\ell+n+1}, g_{\ell+n+2}, \ldots$$

The functions $\phi_1 \ldots \phi_n$ are atomic-like functions corresponding to the atomic state from which the tightly-bound band has evolved.

The functions g_s are now defined and hence also the Bloch functions (2.6). The functions $b_s(\underline{k}, \underline{r})$, $s \leq \ell$, coincide with the crystal core functions and all other crystal eigenfunctions must be orthogonal to these. Thus a suitable set of functions in which to expand $\psi(\underline{k}, \underline{r})$ is obtained by adding linear combinations of the core functions to the remaining Bloch functions $b_s(\underline{k}, \underline{r})$, $s > l$, so as to make them orthogonal to the core functions. The required functions are

$$c_s(\underline{k}, \underline{r}) = g_s(\underline{k}, \underline{r}) - \sum_{\rho=1}^{\ell} \frac{\int g_\rho^* g_s \, d\tau}{\int g_\rho^* g_\rho} g_\rho(\underline{k}, \underline{r}), \quad s > \ell. \tag{2.8}$$

The functions (2.8) are not orthogonal and in fact are linearly dependent as will now be shown. Since the functions $\zeta_s(\underline{r} - \underline{R})$ based on a given lattice site $\underline{R}$ form a complete set of functions, the function $\zeta_t(\underline{r})$ based at the origin may be expressed in the form

$$\zeta_t(\underline{r}) = \sum_s d_{ts}(\underline{R}) \zeta_s(\underline{r} - \underline{R})$$

and using (2.6) it is easy to show that

$$c_s(\underline{k}, \underline{r}) = \exp(-i\underline{k}\cdot\underline{R}) \sum_s d_{ts}(\underline{R}) c_s(\underline{k}, \underline{r}).$$

The functions $c_s(\underline{k}, \underline{r})$ thus form a highly over-complete set in which to expand any function $\psi(\underline{k}, \underline{r})$ which is orthogonal to the core functions. If such an expansion were used in an attempt to solve (2.4) the resulting infinite secular determinant would vanish identically. Even when the infinite determinant is approximated by one of finite size there may still be approximate linear dependence which may make the secular equation practically useless. Parmenter (1952) attempted to use the LCAO method in this form for a calculation of the band occupied by the valence electrons in lithium. He found that to a good approximation all the Bloch functions $c_s(\underline{k}, \underline{r})$ formed from valence and excited atomic functions differed among themselves only by multiplicative constants; they were all very nearly proportional to a single orthogonalized plane wave. Thus

the functions (8) are a very poor set in which to expand wave functions for valence electrons and Fumenter showed that a very much better set is the set of orthogonalized plane waves. Löwdwin (1956) has pointed out that the difficulties arising from linear dependence can in principle be overcome by successively orthogonalising the functions (2.8) but the work involved is prohibitive.

6. The case of d bands

It has been seen that the LCAO method is not suitable for calculating valence bands since the overlap of the atomic functions for valence and excited states on different atoms is so large that the Bloch functions formed from them all approximate closely to a single orthogonalized plane wave. The overlap of atomic d functions in copper and the transition metals, however, is not so large as to cause this difficulty of near linear dependence. The functions $c_s(\underline{k},\underline{r})$ formed from the five degenerate atomic d functions ϕ_1, ϕ_2.... ϕ_5, although not orthogonal, are largely independent. However, the Bloch functions formed from the atomic valence and excited states cannot be used to complete the expansion set owing to their approximate linear dependence. A better choice is to complete the set with plane waves orthogonalized to the core functions and to the functions $c_s(\underline{k}, \underline{r})$, $s = 1.....5$, formed from the d functions ϕ_s. The fifth

order secular equation obtained in the tight-binding method using only the five Bloch functions may thus be regarded as an approximation to the infinite secular equation which would be obtained using a complete set of functions, namely the five Bloch functions and a set of orthogonalized plane waves. It is one of the main purposes of this part of the thesis to examine whether this approximation can yield results of reasonable accuracy.

6.1 The secular equation

The simplifying assumption will now be made that the non-orthogonality of the Bloch functions $b_s(\underline{k}, \underline{r})$, $s > 1$, to the core functions may be neglected. This approximation is made in most existing tight-binding calculations although it should be investigated in any particular case. It is usually a good approximation for reasons discussed in section 6.3.

Thus defining

$$f_m(\underline{k},\underline{r}) = b_{1m}(\underline{k},\underline{r}) = N^{-\frac{1}{2}} \sum_j \exp(i\underline{k}\cdot\underline{R}_j)\phi_m(\underline{r} - \underline{R}_j) \qquad (2.9)$$

approximate solutions of (2.4) are sought of the form

$$\psi(\underline{k}, \underline{r}) = \sum_m a_m(\underline{k})\, f_m(\underline{k}, \underline{r}) \qquad (2.10)$$

On substituting (2.10) in (2.4), multiplying in turn by $f_1^*(\underline{k}, \underline{r})$, $f_2^*(\underline{k}, \underline{r})$ .... $f_5^*(\underline{k}, \underline{r})$, and integrating over the crystal

one obtains the five equations

$$\sum_m a_m(\underline{k}) \{ H_{nm} - E(\underline{k}) \Delta_{nm} \} = 0 \ , \quad n = 1 \ldots 5 , \tag{2.11}$$

where

$$H_{nm} = \int f_n^*(\underline{k}, \underline{r}) \, H \, f_m(\underline{k}, \underline{r}) \, d\tau \tag{2.12}$$

$$\Delta_{nm} = \int f_n^*(\underline{k}, \underline{r}) \, H \, f_m(\underline{k}, \underline{r}) \, d\tau \tag{2.13}$$

Elimination of the $a_m(\underline{k})$ between equations (2.11) yields the secular equation

$$| H_{nm} - E(\underline{k}) \Delta_{nm} | = 0 \ . \tag{2.14}$$

Equations (2.14) has five roots $E_r(\underline{k})$, r = 1, ...5 and to the r^{th} root $E_r(\underline{k})$ there corresponds the approximate wave function

$$\Psi_r(\underline{k},\underline{r}) = \sum_m a_{rm}(\underline{k})\, f_m(\underline{k},\underline{r}) \qquad (2.15)$$

where $a_{r1}(\underline{k}) \cdots a_{r5}(\underline{k})$ satisfy the equations

$$\sum_m a_{rm}(\underline{k}) \{ H_{nm} - E_r(\underline{k})\, \Delta_{nm} \} = 0 \quad , n = 1, \ldots 5 . \qquad (2.16)$$

The secular equations (2.14) can also be obtained by the variational method with a trial function (2.10). If the Bloch functions are orthogonal to the core functions the energies calculated must therefore lie above the true ones.

6.2 Evaluation of the matrix elements

On substituting form (2.9) into (2.12) one obtains

$$H_{nm} = \sum_{s,t} N^{-1} \exp[i\underline{k}.(\underline{R}_s - \underline{R}_t)] \int \phi_n^*(\underline{r}-\underline{R}_t)\, H\, \phi_m(\underline{r}-\underline{R}_t)\, d\tau$$

$$= \sum_t e^{-i\underline{k}.\underline{R}_t} \int \phi_n^*(\underline{r}-\underline{R}_t)\, (-\nabla^2 + V)\, \phi_m(\underline{r})\, d\tau . \qquad (2.17)$$

Also since ϕ_m satisfies the equation

$$[-\nabla^2 + U(r)]\,\phi_m(\underline{r}) = E_0\,\phi_m(\underline{r}) \tag{2.18}$$

equation (2.17) may be written

$$H_{nm} = \sum_t e^{-i\underline{k}\cdot\underline{R}_t} \int \phi_n^*(\underline{r}-\underline{R}_t)(E_0+V-U)\phi_m(\underline{r})\,d\tau$$

$$= E_0 \sum_t S_t^{(nm)} e^{-i\underline{k}\cdot\underline{R}_t} + \sum_t J_t^{(nm)} e^{-i\underline{k}\cdot\underline{R}_t} \tag{2.19}$$

where

$$J_t^{(nm)} = \int \phi_n^*(\underline{r}-\underline{R}_t)[V(\underline{r})-U(r)]\phi_m(\underline{r})\,d\tau \tag{2.20}$$

$$S_t^{(nm)} = \int \phi_n^*(\underline{r}-\underline{R}_t)\,\phi_m(\underline{r})\,d\tau\,. \tag{2.21}$$

Similarly

$$\Delta_{nm} = \sum_t e^{-i\underline{k}\cdot\underline{R}_t}\, S_t^{(nm)} \tag{2.22}$$

and hence

$$H_{nm} - E\Delta_{nm} = (E_0 - E)\sum_t e^{-i\underline{k}\cdot\underline{R}_t} S_t^{(nm)} + \sum_t e^{-i\underline{k}\cdot\underline{R}_t} J_t^{(nm)} . \tag{2.23}$$

Expression (2.20) for $J_t^{(nm)}$ may be broken down by use of (2.1) and in a typical case when $R_t \neq 0$, one obtains

$$\begin{aligned} J_t^{(nm)} = & \int \phi_n^*(\underline{r}-\underline{R}_t)\,[v(\underline{r}) - U(r)]\,\phi_m(\underline{r})\,d\tau \\ & + \int \phi_n^*(\underline{r}-\underline{R}_t)\,v(\underline{r}-\underline{R}_t)\,\phi_m(\underline{r})\,d\tau \\ & + \sum_{i\neq 0,t} \int \phi_n^*(\underline{r}-\underline{R}_t)\,v(\underline{r}-\underline{R}_i)\,\phi_m(\underline{r})\,d\tau . \end{aligned} \tag{2.24}$$

The evaluation of the matrix elements thus consists in evaluating the non-orthogonality integrals $S_t^{(nm)}$, the first two integrals in (2.24) which are two-centre integrals, and the three-centre integrals of the last term of (2.24). Integrals of all these types have been evaluated in the detailed calculation of Chapter 5.

Once the matrix elements have been determined as functions of $\underline{k}$ the determination of the band structure reduces to solving the 5 x 5 secular equation (2.14) at a large number of points in $\underline{k}$-space.

2.3 The crystal potential

The above discussion refers particularly to a 'muffin-tin' form of crystal potential since this form of potential has very

considerable advantages for a tight-binding calculation. A great advantage of the 'muffin-tin' potential is the practical one that the sum of three-centre integrals in (2.24) is rapidly convergent. This is because $v(\underline{r} - \underline{R}_l)$ is non-zero only within a sphere surrounding the lattice site $\underline{R}_l$ and within this region the product

$$\phi^*_n(\underline{r} - \underline{R}_t)\, \phi_m(\underline{r}) \qquad (2.25)$$

is very small if $\underline{R}_l$ is far removed from $\underline{R}_t$ and the origin. Also the three-centre integrals have only to be evaluated over a sphere surrounding a given lattice site $\underline{R}_l$ and expansions of the product (2.25) may be made which only need be valid over this limited region. Use of the 'muffin-tin' potential makes it practicable to calculate all integrals which make a significant contribution to (2.24) and such a calculation has been attempted in the work described in Chapter 5. It must be mentioned that with a 'muffin-tin' potential and a sufficiently large lattice constant (compared with the atomic radius) even the largest three-centre integrals are negligible compared with the two-centre nearest neighbour energy integrals. This is because even if the potential centre $\underline{R}_l$ is a nearest neighbour of both the wave function centres $\underline{R}_0$, $\underline{R}_t$, the product of (2.5) is only appreciable in the outermost regions of the sphere surrounding $\underline{R}_l$, where the potential is practically zero.

The 'muffin-tin' potential has another property which, although it turns out to have no special value in the case of 3d band calcul-

ations, may sometimes be useful and seems worth mentioning. This property is that the potential is spherically symmetric within each unit cell and the useful consequence is that the 'atomic' potential may be chosen so that the trial Bloch functions are very nearly orthogonal to the core functions. This consequence follows since the atomic potential U(r) may be chosen equal to v(r) within the core region and the atomic-like functions ϕ_λ are then orthogonal to the core functions on the same atom. Non-orthogonality of the trial Bloch functions to the core functions then arises only from overlap integrals between ϕ_λ and core functions on neighbouring atoms and these are generally small enough to be neglected. This has already been assumed in section 6.1. It should be mentioned that Bloch functions formed from 3d atomic functions in cubic crystals are always nearly orthogonal to the core functions no matter how the crystal potential V(r) and the 'atomic' potential U(r) are chosen. This is because V(r) has cubic symmetry and the s-like and p-like core functions on a given atom belong to the representations Γ_1 and Γ_{15} respectively, of the cubic group whereas the 3d atomic functions belong to Γ_{12} and Γ_{25}'. Hence the 3d functions ϕ_λ are always orthogonal to the core functions on the same atom and it follows as before that the Bloch functions (2.9) are very nearly orthogonal to the core functions. The functions (2.9) are in fact exactly orthogonal to the core functions at certain symmetry points, and along certain symmetry lines, in the Brillouin zone. This

is pointed out in more detail for the face-centred cubic case in section 10.

Some practical advantages of a 'muffin-tin' potential for a tight-binding calculation have been indicated and in section 8 this type of potential is shown to be the best choice from the point of view of obtaining accurate results. The fact that the potential is taken as constant between spheres is of course a restriction, but since self-consistent potentials are in any case not available this is not unreasonable. The APW and Green's function methods of band structure calculation are also restricted to the 'muffin-tin' type of potential and its reasonableness has recently been argued by Ham and Segall (1961).

6.4 The 'atomic' potential

The choice of the 'atomic' potential U(r) which occurs in equation (2.7) is to some extent arbitrary. However it was pointed out in the previous section that it is often convenient to choose U(r) as equal to v(r) within the core region, although not necessarily the case when one is calculating the structure of d bands. In fact the considerations of section 8.3 show that to obtain accurate results it is usually essential to choose U(r) equal to v(r) within the 'muffin-tin' sphere, although U(r) may differ from v(r) outside this sphere. In section 8.5 a definite criterion is developed which restricts the choice of U(r).

2.5 Crystal field effects

In previous sections it has been pointed out that the 'muffin-tin' form of potential is a convenient one for a tight-binding calculation. However the tight-binding method is by no means restricted to this type of potential, although it is argued in Chapter 3 that the method is most accurate for such a potential. A characteristic of a 'muffin-tin' potential is spherical symmetry within the unit cell and it may sometimes be felt that this does not correspond exactly to the physical situation. In particular Mott and Stevens (1957) have suggested that the non-spherical component of the cubic field in body-centred iron could be sufficient to split the d band into two sub-bands, one formed from d orbitals of Γ_{25}' (xy, yz, zx) symmetry and the other from orbitals of Γ_{12} ($x^2 - y^2$, $3z^2 - r^2$) symmetry (t_{2g} and e_g respectively in another notation). A non-spherical component of potential about each lattice site is readily introduced into a tight-binding calculation and its main effect is on the $\underline{k}$-independent terms.

$$J_o^{(nn)} = \int |\phi_n(\underline{r})|^2 [V(\underline{r}) - U(r)] d\tau \qquad (2.26)$$

which appear in diagonal matrix elements (2.23). $J_o^{(nn)}$ takes two distinct values, one for ϕ_n of Γ_{25}' symmetry and another for ϕ_n of Γ_{12} symmetry, and the effect of this is to shift relative to each other the bands formed from the two types of orbital. These

values are distinct even when V is spherically symmetric within the unit cell, because of the overlap of ϕ_n into neighbouring cells. This type of splitting is evaluated for a particular case in section 17.2; it is always much smaller than the band width. The splitting to be discussed here is due to a non-spherical component of potential $v'(\underline{r})$ and may be written

$$\Delta E = \int \left[|\phi(\Gamma_{25}')|^2 - |\phi(\Gamma_{12})|^2 \right] v'(\underline{r})\, d\tau . \qquad (2.27)$$

Callaway and Edwards (1960) evaluated this expression with

$$v'(\underline{r}) = -\sum_t 2Z/|\underline{r} - \underline{R}_t| + \text{constant} \qquad (2.28)$$

where the constant is an infinite one which exactly cancels the divergence in the summation. This corresponds physically to a case with Z electrons in sp bands whose charge is assumed to be distributed uniformly. It is implicitly assumed that the d electrons do not contribute to the non-spherical component of potential; this may be far from the truth in iron. Nevertheless ΔE was calculated with analytic atomic wave functions for iron and copper, the results being -0.1% e.v. at the observed interatomic spacing for iron and -0.03% e.v. for copper. Certainly in the case of copper, where it is reasonable to take Z = 1, the cubic field splitting is negligible compared with the band width and no splitting into sub-bands will occur.

7. Review of existing tight-binding calculations

The tight-binding method was first introduced by Bloch (1928) and has since been used extensively, particularly in connection with the alkali halides, graphite, the semiconductors of group 4 and the 3-5 compounds, and d bands in the transition metals. The latter application is of most relevance here and existing calculations are reviewed critically below.

7.1 d band calculations

The first application of the tight-binding method to d bands was made by Jones and Mott (1937). They made the simplification of neglecting the non-diagonal matrix elements H_{mn} between Bloch sums formed from functions of xy, yz, zx symmetry and those formed from functions of $x^2 - y^2$, $3z^2 - r^2$ symmetry. In this way the fifth order secular equation conveniently factorises into a cubic and a quadratic, and in a preliminary calculation for nickel Fletcher and Wohlfarth (1951) made the same approximation.

The first proper treatment of d bands was given by Fletcher (1952) for the case of nickel. This calculation extended the preliminary calculation referred to by including the non-diagonal matrix elements which were previously neglected. Fletcher made the two-centre nearest neighbour approximation in which all three-centre and non-orthogonality integrals are neglected, as are all two-centre

energy integrals beyond nearest neighbours. Owing to the use of very localized atomic functions this approximation is probably quite a good one. Fletcher was able to obtain a density of states curve which shows a peak near the top of the band; the value of the linear low temperature electronic heat coefficient deduced from this curve is in good agreement with experiment. The total band width is found to be 2.7 e.v.

Although this calculation was a significant improvement over previous ones it may be criticised in several respects. In the first place the crystal potential is not clearly defined. In calculating the two-centre integral (2.20) it was assumed that $V - U = 0$ within the sphere inscribed in the unit cell about the origin and that

$$V - U(r) = U(\underline{r} - \underline{R}_t)$$

outside this sphere. This assumption may be interpreted roughly as the use of a 'muffin-tin' potential with $V = U$ within each sphere. However the effective neglect of $U(r)$ outside the central sphere in the two-centre integral is then difficult to justify. The effect of its inclusion would be to reduce the integrals in magnitude and shrink the band width which is already quite small. A second criticism is that the 'atomic' functions are not eigenfunctions calculated in the 'atomic' potential. The 'atomic' functions were taken as the Hartree-Fock 3d functions for the Cu^+ ion (Hartree and Hartree 1936) and the

'atomic' potential was taken as the potential arising from the core and a $(3d)^{10}$ configuration. The band structure calculated does not correspond therefore to a crystal potential constructed from the assumed 'atomic' potential; it corresponds more closely to a crystal potential constructed from 'atomic' potentials for which the Hartree-Fock functions are eigenfunctions. This type of uncertainty arising from an insufficiently careful choice of 'atomic' functions and potentials is typical of many tight-binding calculations.

Belding (1959) has carried out tight-binding calculations for the 3d band in chromium, body-centred iron and nickel. 'Atomic' functions were taken to be the interpolated analytic self-consistent field functions given by Löwdin and Appel (1956). Belding followed Fletcher's method very closely and the results are accompanied by the same uncertainties. Belding's work differs from Fletcher's in that two-centre energy integrals beyond nearest neighbours are included. In the case of chromium and nickel neighbours up to the fourth nearest are considered and in the case of iron nearest and next nearest neighbours are included. The effect of third and fourth nearest neighbours is small in all cases and in nickel the next nearest neighbour integrals are only 10% of the nearest neighbour ones. In iron and chromium, however, the second nearest neighbour integrals are about half the size of the nearest neighbour ones and certainly cannot be neglected. For these two metals the neglect of three-centre and non-orthogonality integrals must be very serious. No detailed

results are given apart from a rather crude density of states curve for iron. This shows two main peaks, a large one at the top of the band as in Fletcher's curve and a smaller one nearer the bottom. Due to the effect of second nearest neighbour integrals there is a long tail, 1.01 e.v. long, at the bottom of the band with very low density of states. A similar tail of 1.57 e.v. was found for chromium. The total band width in iron is about 4.7 e.v.

Asdente and Friedel (1961) have calculated a density of states curve for chromium using a 'muffin-tin' type of potential. 'Atomic' functions and the 'atomic' potential were constructed very simply using Slater's (1930) rules and first and second nearest neighbour two-centre energy integrals are included. A band width of about 7.5 e.v. is obtained when the published results are corrected by a factor 2. (This correction is indicated in an erratum note circulated by Asdente).

It is clear that a number of tight-binding calculations in the past have suffered from inconsistencies in the choice of 'atomic' functions and potential. The whole question of this choice in the case of d bands is carefully considered in Chapter 4. Stern (1959) did treat this problem carefully in his calculation for body-centred iron and his modified tight-binding method is an interesting one. Stern used atomic functions calculated for the $3d^7 4s$ configuration in the free

atom and a potential consistent with this choice of atomic function was used in each cell. Stern only considered lines of symmetry in the zone where the relevant Bloch sums can be written down immediately. His modification of the tight-binding method is to expand the Bloch sum in spherical harmonics within a single unit cell and to calculate the expectation energy by integration over this cell, which is approximated by a sphere for the purpose. In this way explicit consideration of multi-centred integrals is avoided. Stern's main approximations are to consider only nearest and next neighbours in the expansion of the Bloch sum, to retain only spherical harmonics with $l \leq 2$, and to expand the radial functions, apart from the central d function, in powers of r up to r^2 only. The truncation of the spherical harmonic expansion appears to be a serious approximation since expansions of the exponentially decreasing radial functions on neighbouring sites are quite slowly convergent. If similar approximations are made the difficulty of calculating the three-centre integrals of the normal tight-binding procedure, which Stern avoids, is greatly reduced. Stern orthogonalizes the expanded Bloch sums to the core functions and normalizes them. Since the approximate expanded Bloch sum is no longer an exact Bloch function, a surface correction term has to be introduced over the surface of the atomic sphere in the calculation of the energy. Stern found a band width of 0.2 e.v.. His main aim was to calculate the cohesive energy and he obtained a value in good agreement with experiment.

Some attention must now be given to the tight-binding interpolation method. This was introduced by Slater and Koster (1954) to interpolate between energies known at symmetry points in the zone. The integrals appearing in the matrix elements of the tight-binding method are expressed in terms of the smallest number of independent integrals, which are treated as disposable parameters. These are chosen so that the energies calculated agree with the known energies at symmetry points. The number of Bloch sums used and the particular approximation (two-centre, nearest neighbour etc.) used for the matrix elements depends on the number of accurately known energies available. Slater and Koster applied the method to d bands in copper, using known energies from Howarth's (1953) cellular calculation, and in iron. They also applied it to diamond and here it is of more doubtful validity, since the approximations of the tight-binding method are probably not valid. Wohlfarth and Cornwell (1961) have used the method to obtain a very detailed density of states curve from Wood's (1962) results on iron. Of course the interpolation method does not yield wave functions.

7.2 Other calculations

Apart from d bands, the main applications of the tight-binding method have been to ionic crystals, semiconducting compounds and graphite. Since very adequate reviews exist [Löwdin (1956, 1962),

Herman(1958), Pincherle(1960)] attention will only be drawn to what appear to be the two most complete calculations. These are Howland's (1958) calculation on the valence band of potassium chloride and Corbato's (1960) work on graphite. The valence band in KCl was found to have a width of only 1.5 e.v, and valence bands in ionic crystals are obviously very suitable subjects for tight-binding calculations. The same cannot really be said of the semi-conductors of group 4, and the 3-5 compounds, or of graphite. The OPW method is better adapted to these materials. In his calculation on two-dimensional graphite Corbato was forced to calculate integrals up to ninth nearest neighbours. The calculation was carried through very rigorously and all significant two-centre, three-centre and non-orthogonality integrals were calculated. However, because of the slow convergence, which is due to the rather extended atomic functions involved, and the restricted set of Bloch sums used, the arguments of the next chapter suggest that the results may not be very accurate.

CHAPTER 3

ERROR IN THE TIGHT-BINDING METHOD AND ITS CORRECTION

There are two main sources of error in a tight-binding calculation. The first of these is that the calculation of the matrix elements (2.24) may be oversimplified, for example by making the two-centre nearest neighbour approximation. The error incurred in this way is not too difficult to estimate and, with some effort, may be eliminated. This may be extremely laborious, as the work of Chapter 5 shows, but there is no difficulty in principle. A more difficult problem is to deal with the second and more fundamental source of error. This arises through using trial wave functions which are simply linear combinations of Bloch functions formed from a restricted set of atomic functions, or even single Bloch functions formed from a non-degenerate atomic function. It was pointed out in section 6 that this set of trial functions may in principle be completed by a set of orthogonalized plane waves, but if carried out straight-forwardly the calculation would then involve solving large secular equations and the essential simplicity of the tight-binding method would be lost. It is one of the aims of this chapter to develop a comparatively simple method of calculating corrections to results obtained using the normal tight-binding trial functions. The terms thus calculated also include

automatically corrections for any non-orthogonality of the trial functions to the core functions. This correction method is developed in section 10 and the interesting form of the correction to the wave function is discussed in section 10.4.

Section 8 deals with a method of obtaining an upper bound to the error in a tight-binding calculation and it is stressed that accuracy depends on a suitable choice of the form of crystal potential and on a suitable choice of 'atomic' potential. In section 9 the error in the tight-binding method is calculated explicitly for a simple model, and in section 11 it is verified that the method of section 10 leads to the proper correction. An important conclusion of this chapter is that the tight-binding method is only likely to be accurate in cases where the nearest neighbour approximation is quite a good one.

8. Errors and Potentials

8.1 Asymptotic Validity of the Tight-binding Method

The essence of the tight-binding method is normally thought to be that asymptotically exact results are obtained as the inter-atomic distance tends to infinity. However, this is only true under certain circumstances as the following example makes clear.

Consider a lattice of point charges Ze with a uniform negative screening charge so that the whole system is electrically neutral. Assume for simplicity that the lattice has cubic symmetry. The

potential energy of an electron at any point $\underline{r}$ is, in atomic units

$$V_d(\underline{r}) = -\sum_t 2Z/|\underline{r}-\underline{R}_t| + \text{constant} \tag{3.1}$$

where the summation is over lattice points $\underline{R}_t$ and the constant is an infinite one, arising from the uniform screening charge, which exactly cancels the divergence in the lattice sum. The subscript d in $V_d(\underline{r})$ indicates the distance between nearest neighbours which may be regarded as a variable. The vectors $\underline{R}_t$ are then functions of d. Suppose that $\phi(\underline{r})$ is the wave function, and E_o the eigenvalue, for a bound s-state in the atomic potential $-2Z/r$. Then the simplest tight-binding approximation for a crystal wave function in the band arising from this atomic state is the Bloch function

$$\psi(\underline{k},\underline{r}) = N^{-\frac{1}{2}} \sum_t e^{i\underline{k}\cdot\underline{R}_t} \phi(\underline{r}-\underline{R}_t) . \tag{3.2}$$

$\phi(r) \sim e^{-\alpha r}$ for large r, where $\alpha^2 = -E_o$, and $\psi(\underline{k},\underline{r})$ is correctly normalized apart from a factor $1 + O(e^{-\alpha d})$. For large d this factor is

$$1 - \tfrac{1}{2} \sum_s e^{i\underline{k}\cdot\underline{\rho}_s} \int \phi^*(\underline{r}-\underline{\rho}_s)\phi(\underline{r})\,d\tau$$

where the summation is over sites $\underline{\rho}_s$ which are nearest neighbours to the site at the origin. The energy corresponding to $\psi(\underline{k},\underline{r})$

is

$$E'_d(\underline{k}) = E_0 + \int |\phi(\underline{r})|^2 \left[V_d(\underline{r}) + \frac{2Z}{r}\right] d\tau$$
$$+ \sum_s e^{i\underline{k}\cdot\underline{\rho}_s} \left[\int \phi^*(\underline{r}-\underline{\rho}_s)\left[V_d(\underline{r}) + \frac{2Z}{r}\right]\phi(\underline{r})\, d\tau \right.$$
$$\left. - \int \phi^*(\underline{r}-\underline{\rho}_s)\,\phi(\underline{r})\, d\tau \int |\phi(\underline{r})|^2 \left[V_d(\underline{r}) + \frac{2Z}{r}\right] d\tau\right], \qquad (3.3)$$

Throughout this chapter a prime on a symbol representing an energy denotes that the energy is calculated within the tight-binding approximation. An upper bound to the error in this expression may be written down using the theorem (Kohn 1947) that the error δE in the energy of a normalized approximation Ψ to an eigenstate obeys

$$|\delta E| \leq \frac{\langle \Psi | (H-\bar{E})^2 | \Psi \rangle}{|\Delta E_{min}|}, \qquad (3.4)$$

where $\bar{E}$ is the mean energy of the state Ψ and ΔE_{min} is the energy interval from $\bar{E}$ to the nearest neighbouring eigenvalue of the same symmetry as Ψ. If (3.4) is applied to (3.2) one obtains for large d

$$|\delta E| \leq \frac{N^{-1}}{|\Delta E_{min}|} \int \left| \left[H - E'_d(\underline{k})\right] \sum_t e^{i\underline{k}\cdot\underline{R}_t} \phi(\underline{r}-\underline{R}_t) \right|^2 d\tau$$
$$= \frac{1}{|\Delta E_{min}|} \int \left[E_0 - E'_d(\underline{k}) + V_d(\underline{r}) + \frac{2Z}{r}\right]^2 |\phi(\underline{r})|^2 d\tau \qquad (3.5)$$

where $|\Delta f_{min}|$ tends to a constant as $d \to \infty$. If $V_d(\underline{r}) + 2Z/r$ is expanded in cubic harmonics about the origin the leading term is a fourth order harmonic and in the neighbourhood of the origin

$$V_d(\underline{r}) + 2Z/r \sim d^{-5}$$

for large d. Also from (3.3) it follows that

$$E'_d(\underline{k}) - E_o \sim d^{-5}.$$

Thus from (3.5) it follows that an upper bound to the error in (3.3) is of order d^{-10} so that the first two terms in (3.3), which are independent of k, are asymptotically exact. However, there is no reason for supposing that any reliance can be placed on the crucial third term, which for large d is $O(e^{-\alpha d}) \ll d^{-10}$ and which determines the asymptotic band structure, in particular the band width. To emphasise this point it is instructive to set up an accurate procedure for calculating the asymptotic band structure.

Suppose in (3.2) $\phi(r)$ is replaced by $\chi_d(\underline{r})$ which satisfies the equation

$$\left[-\nabla^2 + w_d(\underline{r})\right] \chi_d(\underline{r}) = \xi_d \chi_d(\underline{r}) \qquad (3.6)$$

where

$$w_d(\underline{r}) = V(\underline{r}) \quad , \quad |\underline{r}| < \rho d$$
$$0 \quad , \quad |\underline{r}| > \rho d \qquad (\tfrac{1}{2} < \rho < 1)$$

and $\mathcal{E}_d \to E_0$ as $d \to \infty$. It is clear that $\chi_d(\underline{r}) \sim e^{-\alpha r}$ for $|\underline{r}| > \rho d$. Then the energy becomes

$$E_d(\underline{k}) = \mathcal{E}_d + \int |\chi_d(\underline{r})|^2 \left[V_d(\underline{r}) - w_d(\underline{r}) \right] d\tau$$
$$+ \sum_s e^{i\underline{k}\cdot\underline{\rho}_s} \int \chi_d^*(\underline{r}) \left[V_d(\underline{r}) - w_d(\underline{r} - \underline{\rho}_s) \right] \chi_d(\underline{r} - \underline{\rho}_s)\, d\tau$$
$$= \mathcal{E}_d + \sum_s e^{i\underline{k}\cdot\underline{\rho}_s} \int \chi_d^* \left[V_d(\underline{r}) - w_d(\underline{r} - \underline{\rho}_s) \right] \chi_d(\underline{r} - \underline{\rho}_s) d\tau$$

for large d, and $E_d(\underline{k}) - \mathcal{E}_d \sim e^{-\alpha d}$. By the same method as before it is readily shown that the error δE in $E_d(\underline{k})$ satisfies the inequality

$$|\delta E| \leq |\Delta E_{min}|^{-1} \left\{ \int |\chi_d(\underline{r})|^2 \left[V_d(\underline{r}) - w_d(\underline{r}) \right]^2 d\tau \right.$$
$$+ \sum_s e^{i\underline{k}\cdot\underline{\rho}_s} \int \chi_d^*(\underline{r}) \left[V_d(\underline{r}) - w_d(\underline{r}) \right]$$
$$\left. \left[V_d(\underline{r}) - w_d(\underline{r} - \underline{\rho}_s) \right] \chi_d(\underline{r} - \underline{\rho}_s)\, d\tau \right\}$$

(8.7)

where $|\Delta E_{\ldots}|$ is independent of d. It follows that $\delta E \sim e^{-2\alpha|d} \ll e^{-\alpha d}$ for large d, so that $E_d(k)$ is asymptotically exact. The type of procedure indicated here for obtaining asymptotically exact energies has recently been applied by Herring (1962) to the H_2^+ ion and, very powerfully, to justify the Heitler-London-Heisenberg spin Hamiltonian. However, it has not previously been invoked in connection with the band structure problem. Of course, the procedure would be very difficult to carry through explicitly for the example considered here. The potential $w_d(r)$ is not spherically symmetric so that equation (3.6) does not separate. Thus, since the simple Bloch function (3.2) is useless for the purpose, there is no easy way of calculating the asymptotic band structure for the crystal potential (3.1). The same difficulty exists for any crystal potential of the form (3.1) in which the atomic potentials v(r) on neighbouring sites overlap. Thus in the limit of large lattice constant the normal tight-binding method is unsuitable for use with a crystal potential contructed from overlapping atomic potentials. However, the 'muffin-tin' type of potential, which has been advocated in Chapter 2 for other reasons, is unobjectionable in this respect and this is a strong reason for using this type of potential in a tight-binding calculation. Of course, for a practical lattice constant, as opposed to the asymptotic limit, the effect of potential overlap, and therefore the error produced by it, may be small compared with the band width. An example of this was discussed in section 6.5. Nevertheless the use of a 'muffin-tin'

potential avoids a possible source of error and has considerable practicaly advantages. For a practical lattice constant the error in the tight-binding method even for a 'muffin-tin' type of crystal potential and without making the two-centre nearest neighbour approximation, may be quite large and a method of calculating correction terms is described in section 10. In section 8.2 an upper bound to this error is examined and in section 8.3 a discussion, ~~which supplements that of section 6.4,~~ is given of the choice of 'atomic' potential.

8.2 An upper bound to the error in the Tight-binding method

Suppose it is desired to calculate the structure of a band derived from an atomic state which for simplicity will be assumed non-degenerate. Suppose the crystal potential

$$V_d(\underline{r}) = \sum_t v_d[\underline{r} - \underline{R}_t(d)] \qquad (8.8)$$

is of 'muffin-tin' form with touching spheres so that $v_d(r)$ is zero outside the sphere inscribed in the unit cell about the origin, i.e. for $r > d/2$. Suppose the 'atomic' potential $U_d(r)$ used in the tight-binding calculation is equal to $v_d(r)$ at least for $r < d/2$ and suppose that the corresponding 'atomic' function and its energy are $\phi_d(r)$ and E_{od} respectively. The band structure given by the tight-binding approximation is then

$$E'_d(\underline{k}) = E_{od} + \int |\phi_d(\underline{r})|^2 [V_d(\underline{r}) - U_d(r)]\, d\tau + \sum_{s\neq 0} e^{i\underline{k}\cdot\underline{\rho}_s} \int \phi_d^*(\underline{r}) [V_d(\underline{r}) - U_d(\underline{r}-\underline{\rho}_s)] \phi_d(\underline{r}-\underline{\rho}_s) d\tau . \tag{3.9}$$

An upper bound to the error in this expression, similar to (3.7), is for large d

$$|\Delta E_{min}|^{-1} \left\{ \int |\phi_d(\underline{r})|^2 [V_d(\underline{r}) - U_d(r)]^2 d\tau + \sum_{s\neq 0} e^{i\underline{k}\cdot\underline{\rho}_s} \int \phi_d^*(\underline{r}) [V_d(\underline{r}) - U_d(r)] [V_d(\underline{r}) - U_d(\underline{r}-\underline{\rho}_s)] \phi_d(\underline{r}-\underline{\rho}_s) d\tau \right\}. \tag{3.10}$$

It is seen that (3.10) is of the same form as $E'_d(\underline{k}) - E_{od}$ except for an additional factor

$$[V_d(\underline{r}) - U_d(r)] / |\Delta E_{min}| \tag{3.11}$$

in the integrands. It is pointed out later that normally this factor ensures that the error is much less than the band width for sufficiently large d. However for the case considered here of a given finite d the factor may not be small compared with unity throughout the region of $\underline{r}$ which contributes significantly to the energy integrals. Thus the error in the simple tight-

binding approximation due to using a single Bloch function can be significant; if d is large enough this error will be bigger than corrections due to second nearest neighbour energy integrals which are of a smaller exponential order. Of course the simple tight-binding approximation is in general invalid if another band overlaps the one considered so that $|\Delta E_{min}|$ becomes very small. However, it may still be valid at points, or along lines, in the Brillouin zone where the wave functions have different symmetries from those of the overlapping band. This is discussed in ~~section 12~~ chapter 4 for the case of an 's' band overlapping the d band and the error (3.10) is actually estimated for this case. (3.10) is a very convenient formula for an upper bound to the error in a tight-binding calculation and should prove useful in many cases.

8.3 The choice of atomic potential

The idea behind the tight-binding approximation is that the trial functions employed are exactly valid as the lattice constant is allowed to tend to infinity. When considering the case of a finite lattice it is well to bear in mind the limiting case for which the Bloch functions used are exact solutions. Consider the 'muffin-tin' potential (3.8) and put

$$v_d(r) = v(r) - v(d/2), \quad r < d/2$$
$$0 \quad , \quad r > d/2$$

where v(r) is a smooth function, defined for all r, and proportional to -1/r for large r. The symbol d has sometimes been used in this section to represent a variable nearest neighbouring distance, but it will now be used only for the particular value for which the band structure is required. The symbol b will be used to represent a variable distance. The crystal potential (5.8) may then be thought of in two ways. It may be regarded as a special case (b = d) of either of the following two potentials;

$$V_{1b} = \sum_t v_d[\underline{r} - \underline{R}_t(b)]$$

$$V_{2b} = \sum_t v_b[\underline{r} - \underline{R}_t(b)]$$

When $b \gg d$ the potential V_{1b} is only non-zero within spheres of radius d/2 which are far removed from each other. In the case of V_{2b}, however, the spheres are allowed to expand as b increases and the potential is always non-zero within spheres inscribed in the expanded unit cells. The relevant atomic potentials as $b \to \infty$ for V_{1b} and V_{2b} are $v_d(r)$ and $v(r)$ respectively. If $\phi_1(r)$ and $\phi_2(r)$ are the corresponding 'atomic' functions the corresponding Bloch functions are

$$\psi_{ib}(\underline{k}, \underline{r}) = N^{-\frac{1}{2}} \sum_t e^{i\underline{k}\cdot\underline{R}_t(b)} \phi_i[\underline{r} - \underline{R}_t(b)],$$

$$i = 1, 2.$$

Use of theorem (3.4) as before shows that $\psi_{1b}(\underline{k},\underline{r})$ and $\psi_{2b}(\underline{k},\underline{r})$ lead to correct band structures as $b\to\infty$ for the crystal potentials V_{1b} and V_{2b} respectively. In the first case the upper bound to the error goes to zero exponentially as the square of the band width, while in the second case the error goes to zero faster than the band width because of a factor of the form (3.11) with $U_d(r) = v(r)$. In the region of $\underline{r}$ which is significant this factor tends to zero as b^{-2}; this is a consequence of the assumption that $v(r)\propto -1/r$ for large r. Thus in connection with the crystal potential (3.8) it would appear quite reasonable to use 'atomic' functions derived either from an 'atomic' potential $v_d(r)$ or $v(r)$; both choices lead to Bloch functions which have the conceptual advantage that they are exact eigenfunctions for well-defined limiting potentials as the lattice constant is allowed to tend to infinity. (Of course both these limits are merely mathematical models within the one-electron scheme. Neither limiting potential bears any relation to the actual physical potential experienced by an electron when the atoms are well-separated, in which situation band theory is inapplicable.) In practice it is desirable to choose the 'atomic' potential which involves least error at the particular lattice constant which applies. This may be done approximately by attempting to minimise (3.10). The summation term in (3.10) is positive or negative for different $\underline{k}$ so that a typical error is

given by

$$|\Delta E_{min}|^{-1} \int |\phi_d(\underline{r})|^2 \left[V_d(\underline{r}) - U_d(r)\right]^2 d\tau$$

where $|\Delta E_{min}|$ takes a typical value for states of the symmetry considered. This latter must not be too small if the tight-binding method is to hold at all. In such a case ΔE_{min} will not vary much for any reasonable choice of U_d and it suffices to minimise

$$\int |\phi_d(\underline{r})|^2 \left[V_d(\underline{r}) - U_d(r)\right]^2 d\tau$$

It is not an easy problem to find the best U_d since it is a self-consistent problem in the sense that ϕ_d depends on U_d in a complicated way. However, it is not so difficult to compare the merits of two given 'atomic' potentials. $[V_d(\underline{r})-U_d(r)]^2$ is larger if $U_d(r)=v(r)$ than if $U_d(r) = v_d(r)$ but on the other hand $v(r)$ is the deeper potential well so that $\phi_d(\underline{r})$ will fall off more quickly with r. This type of criterion should be of assistance in choosing 'atomic' potentials in practice. In nearly all cases it will be advisable to choose $U_d(r) = V_d(\underline{r})$ at least for $r < d/2$ since $|\phi_d(\underline{r})|$ is largest in this

region.

9. Error Term in a Simple Case

Before considering a general method of calculating the error term in a tight-binding calculation it seems worthwhile to consider a simple case for which the tight-binding method can be tested directly. An obvious method of testing any approximate method of band-structure calculation is to carry out such a calculation with a crystal potential for which the band-structure is exactly known. An example of such a test is the 'empty lattice test' used by Shockley (1937) to expose the inadequacies of the original cellular method. Unfortunately exact band structures are only known for the empty lattice and for potentials of the form

$$V(x) + V(y) + V(z)$$

such as in the Mathieu problem considered by Slater (1952). None of these potentials are suitable for a tight-binding calculation and so no analogue of the 'empty lattice test' is possible in three dimensions. It therefore seems worthwhile to consider a one-dimensional crystal potential and a particularly simple one is that of a chain of δ-functions. The band structure for this model can be calculated exactly and in this section the structure of the lowest

band is compared with that calculated by the tight-binding approximation.

Kronig and Penney (1931) considered a crystal potential of the form shown in figure 3a and they obtained the relation between the electron energy $\mathcal{E}$ and the wave-vector k in the form

$$\cos k(a+b) = \cos \beta a \cosh \gamma b + \frac{\gamma^2 - \beta^2}{2\beta\gamma} \sin \beta a \sinh \gamma b \qquad (3.12)$$

where, using atomic units,

$$\beta^2 = \mathcal{E} \quad , \quad \gamma^2 = V_0 - \mathcal{E} \, . \qquad (3.13)$$

It is more convenient for the present purpose to consider the crystal potential shown in figure 3b and electron energy E is then given by (3.12) with

$$\beta^2 = E + V_0 \quad , \quad \gamma^2 = -E \, . \qquad (3.14)$$

For simplicity the detailed calculation to be given here is restricted to the limiting case when $a \to 0$ and $V_0 \to \infty$ so that aV_0 remains finite. In this limit with $aV_0 = 2P$, say, (3.12) becomes

$$\cos kb = \cosh \gamma b - \frac{P}{\gamma} \sinh \gamma b \, . \qquad (3.15)$$

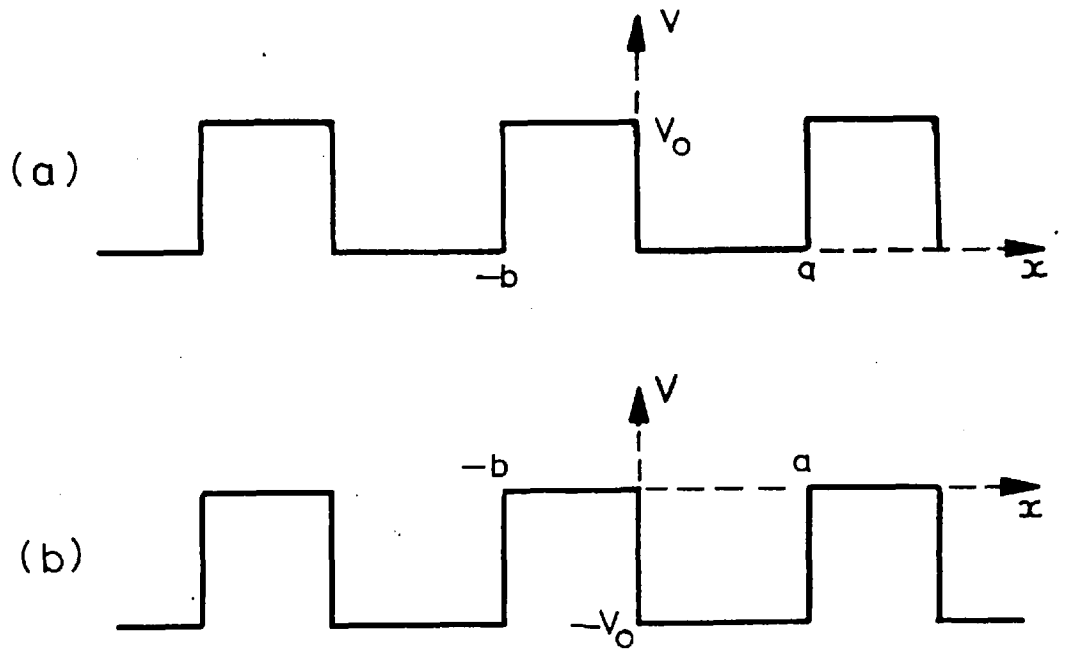

Fig. 3

The crystal potential in this limit is

$$V = -2\rho \sum_{n=-\infty}^{\infty} \delta(x-n\ell) \qquad (3.16)$$

and (3.15) gives the electron energy $E = -\gamma^2$ implicitly as a function of k. (3.16) represents a chain of attractive δ-function potentials and this differs from the limit of a chain of repulsive δ-function potentials which was considered by Kronig and Penney. The present purpose is to find an explicit expression for the electron energy in the lowest band and to compare it with that obtained by the tight-binding method.

The obvious 'atomic' potential to choose in the tight-binding calculation is

$$U = -2P\,\delta(x) \tag{3.17}$$

and the wave function for the bound state in this potential is

$$\phi(x) = \sqrt{P}\; e^{-P|x|} \tag{3.18}$$

with energy

$$E_0 = -P^2 ,$$

The band of interest is therefore that which arises from this 'atomic' level as b decreases from infinity. The electron energy in this band, expressed as a series of ascending powers of e^{-Pb}, may be obtained from (3.15) as follows.

Put

$$E = E_0 + \epsilon , \tag{3.19}$$

that is

$$\gamma^2 = P^2 - \epsilon ,$$

whence for $\epsilon < P^2$

$$\gamma = P - \tfrac{1}{2}\frac{\epsilon}{P} - \tfrac{1}{8}\frac{\epsilon^2}{P^3} - \tfrac{1}{16}\frac{\epsilon^3}{P^5} - \ldots . \tag{3.20}$$

Equation (3.15) may then be written

$$\begin{aligned}\cos kb = {} & \cosh \rho b \cosh\left[\tfrac{1}{2}\frac{\epsilon b}{\rho} + \tfrac{1}{8}\frac{\epsilon^2 b}{\rho^3} + \tfrac{1}{16}\frac{\epsilon^3 b}{\rho^5} + \ldots\right] \\ & - \sinh \rho b \sinh\left[\tfrac{1}{2}\frac{\epsilon b}{\rho} + \tfrac{1}{8}\frac{\epsilon^2 b}{\rho^3} + \tfrac{1}{16}\frac{\epsilon^3 b}{\rho^5} + \ldots\right] \\ & - \left\{1 + \tfrac{1}{2}\frac{\epsilon}{\rho^2} + \tfrac{3}{8}\frac{\epsilon^2}{\rho^4} + \tfrac{5}{16}\frac{\epsilon^3}{\rho^6} + \ldots\right\} \\ & \times \left\{\sinh \rho b \cosh\left[\tfrac{1}{2}\frac{\epsilon b}{\rho} + \tfrac{1}{8}\frac{\epsilon^2 b}{\rho^3} + \tfrac{1}{16}\frac{\epsilon^3 b}{\rho^5} + \ldots\right]\right. \\ & \left. - \cosh \rho b \sinh\left[\tfrac{1}{2}\frac{\epsilon b}{\rho} + \tfrac{1}{8}\frac{\epsilon^2 b}{\rho^3} + \tfrac{1}{16}\frac{\epsilon^3 b}{\rho^5} + \ldots\right]\right\}\end{aligned}$$

and expanding this in powers of ϵ one obtains

$$\begin{aligned}\cos kb = {} & e^{-\rho b} + \epsilon\left[-\frac{1}{4\rho^2} e^{\rho b} + \left(\frac{b}{2\rho} + \frac{1}{4\rho^2}\right) e^{-\rho b}\right] \\ & + \epsilon^2\left[\left(\frac{b}{8\rho^3} - \frac{3}{16\rho^4}\right) e^{\rho b} + \left(\frac{b^2}{8\rho^2} + \frac{b}{4\rho^3} + \frac{3}{16\rho^4}\right) e^{-\rho b}\right] \\ & + \epsilon^3\left[\left(-\frac{b^2}{32\rho^4} + \frac{b}{8\rho^5} - \frac{5}{32\rho^6}\right) e^{\rho b}\right. \\ & \left. + \left(\frac{b^3}{48\rho^3} + \frac{3b^2}{32\rho^4} + \frac{3b}{16\rho^5} + \frac{5}{32\rho^6}\right) e^{-\rho b}\right] \\ & + \ldots .\end{aligned} \tag{3.21}$$

The problem is now to invert (3.21) and obtain ϵ as a series in ascending powers of $e^{-\rho b}$. This may be done by an iterative procedure. Thus the first approximation to ϵ for large ρb is

$$\epsilon_1 = -4\rho^2 e^{-\rho b} \cos kb \tag{3.22}$$

and a second approximation, correct to order $e^{-2\rho b}$ is obtained by substituting ϵ_1^2 for the ϵ^2 in (3.21) and solving for ϵ. A further iteration yields ϵ correct to order $e^{-3\rho b}$ and the result is

$$\epsilon = -4\rho^2 \left\{ e^{-\rho k} \cos hk + e^{-2\rho k} \left[\left(\tfrac{1}{2} - \rho k\right) - \frac{2\rho k - 3}{2} \cos 2hk \right] + e^{-3\rho k} \left[\left(\tfrac{9}{2}\rho^2 k^2 - 6\rho k + 1 \right) \cos hk + \left(\tfrac{3}{2}\rho^2 k^2 - 4\rho k + 2 \right) \cos 3hk \right] \right\} \quad (3.23)$$

The iterative procedure appears to converge as long as $\rho b e^{-\rho b} \ll 1$ and this condition certainly ensures that $\epsilon < \rho^2$.

It follows from equations (2.20), (2.21) and (2.23) that the tight-binding approximation to ϵ is given by

$$\epsilon' = \frac{\sum_{m=-\infty}^{\infty} e^{-ikmb} \int \phi^*(x-mb)\,[V-U]\,\phi(x)\,dx}{\sum_{m=-\infty}^{\infty} e^{-ikmb} \int \phi^*(x-mb)\,\phi(x)\,dx} \quad (3.24)$$

where V, U and ϕ are defined by (3.16), (3.17) and (3.18).

(3.24) may be written as

$$\epsilon' = \frac{\int |\phi(x)|^2 (V-U)\,dx + \sum_{m=1}^{\infty} 2\cos kmb \int \phi^*(x-mb)(V-U)\phi(x)\,dx}{1 + \sum_{m=1}^{\infty} 2\cos kmb \int \phi^*(x-mb)\,\phi(x)\,dx} \quad (3.25)$$

and on evaluating the integrals and neglecting terms which contribute to a higher order than e^{-3Pb} in ϵ , one obtains

$$\epsilon' = \frac{\left[\begin{array}{l} -4\rho^2 e^{-2\rho b} - 4\rho^2 (e^{-\rho b} + 2e^{-3\rho b}) \cos kb \\ \quad - 8\rho^2 e^{-2\rho b} \cos 2kb - 12\rho^2 e^{-3\rho b} \cos 3kb \end{array}\right]}{1 + 2(1+\rho b) e^{-\rho b} \cos kb + 2(1+2\rho b) e^{-2\rho b} \cos 2kb} \qquad (3.26)$$

For $Pbe^{-Pb} \ll 1$, which inequality must hold for the tight-binding approximation to be useful, the denominator may be expanded and ϵ' finally expressed in the form

$$\epsilon' = -4P^2 \{ e^{-\frac{1}{2}Pb} \cos kb + e^{-2Pb} [-Pb - (Pb - 1)\cos 2kb] + e^{-3Pb} [(3P^2b^2 - 2)\cos kb + (P^2b^2 - 2Pb + 1)\cos 3kb] \} \qquad (3.27)$$

A comparison of ϵ' with the exact expression (3.25) shows that the first order term is given exactly by the tight-binding approximation, the second order term is very nearly correct for large Pb but the third order term may be 50% in error for large Pb. The required correction to the tight-binding energy in second order is

$$- 2P^2 e^{-2Pb} (1 + \cos 2kb). \qquad (3.28)$$

The exactness of the first order term could have been predicted from an inequality of the type (3.7). Since the 'atomic' potential used coincides with the crystal potential for $|x| < b$ and the 'atomic' function is $\sqrt{P}\, e^{-P|x|}$ it follows that an upper bound to the error in the tight-binding method is $O(e^{-2Pb})$. It is a very exceptional feature of this example that the 'atomic' potential coincides with the crystal potential right up to the nearest neighbour lattice sites and in a more general case there may be corrections to the first order term,

In the present example, if the tight-binding approximation is used for a lattice constant such that the third order term makes a significant contribution, the results will be unreliable. In a more general case it may well be that second order terms are unreliable and that the tight-binding approximation should be restricted to cases where the nearest neighbour approximation is a good one, so that second order terms are negligible. It is certainly desirable to have a method of calculating corrections to the usual tight-binding approximation and one is described in the next section.

It is easily seen from equation (3.26) that neglect of non-orthogonality integrals would make the e^{-2Pb} term completely wrong.

It is also interesting to note that a three-centre integral makes a contribution to the e^{-2Pb} term already.

10. General Method of Calculating Error Terms

The wave function used in the tight-binding method is either a single Bloch function or a linear combination of Bloch functions formed from a restricted set of atomic functions. The error involved in using this type of wave function is the subject of this section. It has already been pointed out that the normal tight-binding form of wave function could be supplemented by orthogonalized plane waves but this would lead to large secular equations in a straight-forward calculation. In the method to be described the normal trial function is supplemented by a sum of plane waves but a secular equation, other than that which may already exist in the normal tight-binding method, is avoided. It is found possible in a fairly general case to calculate the asymptotically exact correction term by only solving inhomogeneous integral equations, which are not eigenfunction problems.

10.1 Non-degenerate Case

Consider first the case of a band which arises from a non-degenerate atomic function. Suppose the crystal potential is of the 'muffin-tin' form (3.8) but that the spheres, within which the potential is non-zero, do not necessarily touch and are of

radius qd where $q \leqslant \frac{1}{2}$. If the atomic potential $U_d(r)$ is chosen equal to $v_d(r)$ it coincides with $V(\underline{r})$ for $r < pd$ where $p = 1 - q$. Since $0 \leqslant q \leqslant \frac{1}{2}$, $\frac{1}{2} \leqslant p \leqslant 1$. (The possibility $q = 0$ is included to cover the δ-function case). It will be noticed that the 'atomic' potential chosen here varies with the lattice constant and it may be taken in the form

$$U_d(r) = v_d(r) = v(r) - v(qd), \quad r < qd$$
$$0 \qquad\qquad , \quad r > qd \tag{3.29}$$

where $v(r) \longrightarrow 0$ as $r \to \infty$.

The 'atomic' function $\phi_d(\underline{r})$ satisfies the equation

$$[-\nabla^2 + U_d(r)]\, \phi_d(\underline{r}) = E_{od}\phi_d(\underline{r}) \tag{3.30}$$

If $E_{od} \longrightarrow E_o$ as $d \to \infty$, $\phi_d(\underline{r}) \sim e^{-\alpha r}$ for large r where $\alpha^2 = -E_o$. It is required to solve the equation

$$\left[-\nabla^2 + V_d - E_d(\underline{k})\right] \Psi_d(\underline{k}, \underline{r}) = 0 \tag{3.31}$$

and the tight-binding approximation to this solution is

$$f_d(\underline{k},\underline{r}) = N^{-\frac{1}{2}} \sum_j \exp(i\underline{k}\cdot\underline{R}_j)\phi_d(\underline{r} - \underline{R}_j) \quad . \tag{3.32}$$

The tight-binding approximation to $E_d(\underline{k}) - E_{od}$ is of order $e^{-\alpha d}$ and the argument of section 6.2 shows that the correction to this can at most be of the same order; hence $E_d(\underline{k}) - E_{od} \sim e^{-\alpha d}$. From now on it is convenient to drop the suffix d from energies and wave functions. Suppose the exact solution of (3.31) is

$$\psi(\underline{k},\underline{r}) = f(\underline{k},\underline{r}) + \Omega^{-\frac{1}{2}} \sum_s b_s e^{i(\underline{k}+\underline{K}_s).\underline{r}} \tag{3.33}$$

where Ω is the volume of the crystal and the summation is over all reciprocal lattices vectors $\underline{K}_s$. When (3.33) is substituted in (3.30) and the resultant equation is multiplied by $\exp[-i(\underline{k} + \underline{K}_t).\underline{r}]$ and integrated over the crystal volume, one obtains

$$\int e^{-i(\underline{k}+\underline{K}_t).\underline{r}} (-\nabla^2 + V - E) f \, d\tau + \Omega^{\frac{1}{2}} \sum_s b_s \left[\{(\underline{k}+\underline{K}_s)^2 - E\} \delta_{ts} + V_{ts} \right] = 0 \tag{3.34}$$

where

$$V_{ts} = \Omega^{-1} \int e^{i(\underline{K}_s - \underline{K}_t).\underline{r}} V(\underline{r}) \, d\tau = \Delta^{-1} \int e^{i(\underline{K}_s - \underline{K}_t).\underline{r}} U(r) \, d\tau , \tag{3.35}$$

$\Delta = \Omega/N$ being the volume of a unit cell. If (3.32) is used to substitute for f in (3.34), and use is made of (3.30), it is easily shown that

$$\Delta^{-\frac{1}{2}} \int e^{-i(\underline{k}+\underline{K}_t).\underline{r}} [E_0 - E + V - U(r)] \phi(\underline{r}) d\tau + \sum_s b_s [\{(\underline{k}+\underline{K}_s)^2 - E\}\delta_{ts} + V_{ts}] = 0. \qquad (3.36)$$

Since V - U is zero for $r < pd$ and $\phi(\underline{r}) \sim e^{-\alpha r}$ for large r (also $E_0 - E \sim e^{-\alpha d}$) it follows that if the lattice constant is sufficiently large $b_s \sim e^{-\alpha pd}$. The task of solving (3.36) for the coefficient b_s exactly is obviously an impossible one. It would be equivalent to solving the band structure problem exactly by a plane wave expansion and the first term in (3.33) would be an unnecessary encumbrance. However, the lesser task of finding the asymptotic form of $b_s (\sim e^{-\alpha pd})$ when $d \to \infty$ is not too difficult and may be done without solving a secular equation. Even for a finite lattice constant, if it is sufficiently large for the tight-binding approximation to be appropriate, and particularly if the nearest neighbour approximation is a good one, it may be expected that the asymptotic form for b_s leads to an accurate corrected wave function (3.33) and hence to an accurate energy.

The following great simplifications may be made in (3.36) if only the asymptotic form of b_s is required. In the first term $E_0 - E$

may be replaced by the tight-binding approximation to that quantity and in the second term E may be replaced by E_o. These two replacements involve neglecting terms of order $e^{-2\alpha pd}$ and $e^{-\alpha(p+1)d}$ respectively whereas the dominant terms in (3.36) are of order $e^{-\alpha pd}$. Unless p = 1 the $E_o - E$ in the first term may be neglected completely since it is of order $e^{-\alpha d}$. However, it is not inconvenient to retain the tight-binding approximation to it for the present. With the above simplificiations (3.36) becomes

$$\Delta^{-\frac{1}{2}} \int e^{-i(\underline{k}+\underline{K}_t).\underline{r}} \left[E_o - E' + V - U(r)\right] \phi(\underline{r}) d\tau$$

$$+ \sum_s b_s \left[\{ (\underline{k}+\underline{K}_s)^2 - E_o \} \delta_{st} + V_{ts} \right]$$

$$= 0 \qquad (3.37)$$

where E' is the tight-binding approximation to the true eigenvalue of E. It is required to find b_s of order $e^{-\alpha pd}$ such that (3.37) is satisfied to that order. This is no longer an eigenfunction problem. It is very important not to attempt to satisfy (3.37) exactly to all orders since E_o is not an exact eigenvalue in general and the only exact solution of (3.37) for large but finite d is the trivial one with b_s such that $\psi(\underline{k},\underline{r}) = 0$.

With the substitution

$$c_s = \left[(\underline{k} + K_s)^2 - E_o\right] b_s \qquad (3.38)$$

(3.37) becomes

$$\sum_s \frac{V_{ts}\, c_s}{(\underline{k}+\underline{K}_s)^2 - E_0} + c_t$$

$$= -\Delta^{-\frac{1}{2}} \int e^{-i(\underline{k}+\underline{K}_t)\cdot\underline{r}} \left[E_0 - E' + V - U(r)\right] \phi(\underline{r})\, d\tau. \tag{3.39}$$

If a function $\gamma(\underline{k},\underline{r})$ is defined, not uniquely, such that

$$c_s = \Delta^{-1} \int \gamma(\underline{k},\underline{r})\, e^{-i\underline{K}_s\cdot\underline{r}}\, d\tau \tag{3.40}$$

then, by using (3.35), one may write (3.39) as

$$-\iint U(r_1)\, G(\underline{r}_1,\underline{r}_2)\, \gamma(\underline{k},\underline{r}_2)\, e^{-i\underline{K}_t\cdot\underline{r}_1}\, e^{-i\underline{k}\cdot(\underline{r}_1-\underline{r}_2)}\, d\tau_1\, d\tau_2$$

$$+ \int \gamma(\underline{k},\underline{r}_1)\, e^{-i\underline{K}_t\cdot\underline{r}_1}\, d\tau_1$$

$$= \Delta^{\frac{1}{2}} \int e^{-i(\underline{k}+\underline{K}_t)\cdot\underline{r}_1} \left[E_0 - E' + V - U(r_1)\right] \phi(\underline{r}_1)\, d\tau_1 \tag{3.41}$$

where

$$G(\underline{r}_1,\underline{r}_2) = -\Delta^{-1} \sum_s \frac{\exp\left[i(\underline{K}_s+\underline{k})\cdot(\underline{r}_1-\underline{r}_2)\right]}{(\underline{k}+\underline{K}_s)^2 - E_0}\,. \tag{3.42}$$

$G(\underline{r}, \underline{r})$ is the Green function for the operator $(-\nabla^2 - E_0)$ with the periodic boundary conditions (Kohn and Rostocker 1954) and may also be written

$$G(\underline{r}_1, \underline{r}_2) = -\frac{1}{4\pi} \sum_s \frac{\exp[-\alpha|\underline{r}_1 - \underline{r}_2 - \underline{R}_s|]}{|\underline{r}_1 - \underline{r}_2 - \underline{R}_s|} e^{i\underline{k}\cdot\underline{R}_s} . \tag{3.43}$$

If one writes

$$\beta(\underline{k}, \underline{r}) = \Delta^{-\frac{1}{2}} \gamma(\underline{k}, \underline{r}) e^{i\underline{k}\cdot\underline{r}} \tag{3.44}$$

(3.41) is certainly satisfied if

$$U(r_1) \int G(\underline{r}_1, \underline{r}_2) \beta(\underline{k}, \underline{r}_2) d\tau_2 - \beta(\underline{k}, \underline{r}_1) = [E_0 - E' + V - U(r_1)] \phi(\underline{r}_1) . \tag{3.45}$$

(3.45) does not follow uniquely from (3.41) and there is no guarantee that there exists a solution of (3.45) of the required type. It is necessary that $\beta(\underline{k},\underline{r})$ should be of order $e^{-\alpha Rd}$ and should satisfy (3.45) to that order. If, however, such a solution can be found, then retracing the whole argument one is led to b_s of the correct order which satisfy (3.37) to the required

accuracy. In fact it turns out that one can find such a solution; this is shown in section 10.3 and will be assumed for the present.

If $\beta(\underline{k},\underline{r})$ is known it is simple to find the corrected wave function $\psi(\underline{k},\underline{r})$ and energy $E(\underline{k})$. From (3.38), (3.40) and (3.44) it follows that

$$\beta_s = \Delta^{-\frac{1}{2}} \frac{\int \beta(\underline{k},\underline{r}) \exp\left[-i(\underline{k}+\underline{K}_s).\underline{r}\right] d\tau}{(\underline{k}+\underline{K}_s)^2 - E_0} \tag{3.46}$$

and hence (3.33) becomes

$$\psi(\underline{k},\underline{r}) = f(\underline{k},\underline{r}) + \frac{1}{\Delta N^{1/2}} \sum_s \int \frac{\beta(\underline{k},\underline{r}') \exp\left[i(\underline{k}+\underline{K}_s).(\underline{r}-\underline{r}')\right]}{(\underline{k}+\underline{K}_s)^2 - E_0} d\tau'$$

$$= f(\underline{k},\underline{r}) - N^{-\frac{1}{2}} \int G(\underline{r},\underline{r}') \beta(\underline{k},\underline{r}') d\tau' . \tag{3.47}$$

This wave function, although not exactly normalized, is correct to order $e^{-\alpha pd}$. The energy is simply derived from the following equation obtained by substituting (3.33) in (3.31), multiplying by $f^*(\underline{k},\underline{r})$, integrating over the crystal volume and using (3.32) and (3.30):

$$\int f^* (-\nabla^2 + V) f \, d\tau - E \int f^* f \, d\tau$$

$$+ \Delta^{-\frac{1}{2}} \sum_s \beta_s \int e^{i(\underline{k}+\underline{K}_s).\underline{r}} \left[E_0 - E + V - U(r)\right] \phi^*(\underline{r}) d\tau$$

$$= 0 .$$

$E_o - E$ in the last term may be replaced by $E_o - E'$, or neglected unless $p = 1$, and E is then obtained, correct to order $e^{-2\alpha pd}$, in the form

$$E = \frac{\int f^*(-\nabla^2+V)f\,d\tau}{\int f^* f\,d\tau} + \Delta^{-\frac{1}{2}} \sum_s \rho_s \int e^{i(\underline{k}+\underline{K}_s).\underline{r}} [E_o - E' + V - U(r)]\phi^*(\underline{r})d\tau$$

$$= E' - \iint \beta(\underline{k},\underline{r}')\, G(\underline{r},\underline{r}')\,[E_o - E' + V - U(r)]\,\phi^*(\underline{r})\,d\tau d\tau' \qquad (3.48)$$

where use is made of (3.46) and (3.42). A discussion of formulae (3.47) and (3.48) is given in section 10.4. The method developed in this section for solving the band structure problem exactly in the limit of large lattice constant may be regarded as a combination of the tight-binding method and the Green function method (Kohn and Rostocker 1954). In the next section the work so far is generalized to the degenerate case.

10.2 Degenerate case

Consider now the case of bands which arise from a set of degenerate 'atomic' functions. The problem may be formulated exactly as before except that there are now a number of 'atomic' functions $\phi_n(\underline{r})$ satisfying (3.30) and the tight-binding approximation to the crystal wave function is of the form

$$\sum_n a_n f_n(\underline{k},\underline{r}),$$

where $f_n(\underline{k},\underline{r})$ is the Bloch function (3.32) formed from $\phi_n(\underline{r})$. Suppose an exact solution of (3.31) is

$$\psi(\underline{k},\underline{r}) = \sum_n a_n f_n(\underline{k},\underline{r}) + \Omega^{-\frac{1}{2}} \sum_s B_s e^{i(\underline{k}+\underline{K}_s).\underline{r}} . \tag{3.49}$$

Following the method of the non-degenerate case one then obtains the following equivalent of equation (3.37):

$$\Delta^{-\frac{1}{2}} \sum_n a_n \int e^{-i(\underline{k}+\underline{K}_t).\underline{r}} [V - U(r)] \phi_n(\underline{r}) d\tau + \sum_s B_s \left[\{(\underline{k}+\underline{K}_s)^2 - E_o\} \delta_{st} + V_{ts} \right] = 0 . \tag{3.50}$$

The term corresponding to the $E_o - E'$ term in the integrand of the first term in (3.37) is omitted here for convenience although it could be included. If b_{ns} is defined as a quantity of order $e^{-\alpha pd}$ which satisfies

$$\Delta^{-\frac{1}{2}} \int e^{-i(\underline{k}+\underline{K}_t).\underline{r}} [V - U(r)] \phi_n(\underline{r}) d\tau + \sum_s b_{ns} \left[\{(\underline{k}+\underline{K}_s)^2 - E_o\} \delta_{st} + V_{ts} \right] = 0 \tag{3.51}$$

correct to the same order, then the required solution of (3.50) is

$$B_s = \sum_n a_n b_{ns} . \tag{3.52}$$

Following the method of section 10.1 it is possible to express b_{ns} in the form

$$b_{ns} = \Delta^{-\frac{1}{2}} \frac{\int \beta_n(\underline{k},\underline{r}) \exp[-i(\underline{k}+\underline{K}_s).\underline{r}]\,d\tau}{(\underline{k}+\underline{K}_s)^2 - E_0} \tag{3.53}$$

where $\beta_n(\underline{k},\underline{r})$ is of order $e^{-\alpha r_d}$ and satisfies

$$U(r_1)\int G(\underline{r}_1,\underline{r}_2)\beta_n(\underline{k},\underline{r}_2)\,d\tau_2 - \beta_n(\underline{k},\underline{r}_1) = [V-U(\underline{r}_1)]\phi_n(\underline{r}_1) \tag{3.54}$$

to that order. The energy is obtained as follows. Substitute (3.49) in (3.31), multiply by f_m^*, integrate over the crystal volume, use (3.32), (3.30) and (3.52) and thus obtain

$$\sum_n a_n \Big\{ \int f_m^* (-\nabla^2 + V - E) f_n \,d\tau + \Delta^{-\frac{1}{2}} \sum_s b_{ns} \int e^{i(\underline{k}+\underline{K}_s).\underline{r}} [V-U(r)]\phi_m^*(\underline{r})\,d\tau \Big\} = 0 .$$

Eliminating the a_n one obtains a secular equation which is just the usual secular equation of the tight-binding method in the degenerate case but with additional terms in the matrix elements. These additional terms may be expressed in terms of the $\beta_n(\underline{k},\underline{r})$

as in (3.48). Thus once the integral equations (3.54) have been solved a corrected secular equation may be set up which must then be solved in the usual way.

10.3 The integral equation

Integral equations of the type (3.45) and (3.54) must now be considered in some detail. Since $U(r) = 0$ for $r > qd$ it is immediately obvious that

$$\beta(\underline{k}, \underline{r}_1) = -[E_0 - E' + V - U(r_1)]\phi(\underline{r}_1), \quad r_1 > qd. \tag{3.55}$$

To consider the solution of (3.45) for $r_1 < qd$ it is convenient to use expression (3.43) for $G(\underline{r}_1, \underline{r}_2)$ and thus obtain

$$\frac{U(r_1)}{4\pi} \sum_S e^{i\underline{k}\cdot\underline{R}_S} \int \frac{e^{-\alpha|\underline{r}_1 - \underline{r}_2 - \underline{R}_S|}}{|\underline{r}_1 - \underline{r}_2 - \underline{R}_S|} \beta(\underline{k}, \underline{r}_2)\, d\tau_2 + \beta(\underline{k}, \underline{r}_1)$$
$$= -[E_0 - E']\phi(\underline{r}_1)$$

which may be written

$$\frac{U(r_1)}{4\pi} \int \frac{e^{-\alpha r_{12}}}{r_{12}} \left\{ \beta(\underline{k}, \underline{r}_2) + \sum_{S \neq 0} e^{i\underline{k}\cdot\underline{R}_S} \beta(\underline{k}, \underline{r}_2 - \underline{R}_S) \right\} d\tau_2$$
$$+ \beta(\underline{k}, \underline{r}_1) = -[E_0 - E']\phi(\underline{r}_1) \tag{3.56}$$

where $r_{12} = |\underline{r}_1 - \underline{r}_2|$.

Consider the first case when $0 < q < \frac{1}{2}$ (i.e. $q \neq \frac{1}{2}$) so that the spheres in the 'muffin-tin' potential do not touch. Then because of the $e^{-\alpha r_{12}}$ term in the integrand of the first term of (3.56), and since the $U(r_1)$ factor ensures that this term vanishes for $r_1 > qd$, it is sufficient to substitute the exterior solution (3.55) for $\beta(\underline{k}, \underline{r}_2 - \underline{R}_s)$. The equation is then correct to order $e^{-\alpha pd}$, and the $E_0 - E'$ terms may be neglected if only terms of this order are retained. To this order (3.56) becomes

$$\frac{U(r_1)}{4\pi} \int \frac{e^{-\alpha r_{12}}}{r_{12}} \beta(\underline{k}, \underline{r}_2) d\underline{r}_2 + \beta(\underline{k}, \underline{r}_1) = \frac{U(r_1)}{4\pi} \sum_{s \neq 0} e^{i \underline{k} \cdot \underline{R}_s} \int \frac{e^{-\alpha r_{12}}}{r_{12}} U(r_2) \phi(\underline{r}_2 - \underline{R}_s) d\underline{r}_2 \qquad (3.57)$$

where the integrations are over $r_2 < qd$.

A difficulty now appears but it proves to be more apparent than real. Suppose one attempts to solve the inhomogeneous integral equation (3.57) by expanding β in terms of the eigenfunctions q_λ of the homogeneous integral equation

$$-\lambda \frac{U(r_1)}{4\pi} \int \frac{e^{-\alpha r_{12}}}{r_{12}} q_\lambda(r_2) d\underline{r}_2 = q_\lambda(\underline{r}_1). \qquad (3.58)$$

Now the homogeneous equation obtained from (3.57) by setting the right-hand side equal to zero is just (3.58) with $\lambda = 1$. It follows [Morse and Feshbach (1953) pp.959-60] that if $\lambda = 1$ is an eigenvalue of (3.58) there is no solution of (3.57) unless the right hand side of that equation is orthogonal to the eigenfunction q_1. Now $\lambda = 1$ is in fact an eigenvalue of (3.58) with eigenfunction $q_1(\underline{r}) = U(r)\,\phi\,(\underline{r})$ since ϕ satisfies the integral equation formulation of the atomic eigenvalue problem (3.30), viz.

$$-\frac{1}{4\pi}\int \frac{e^{-dr_{12}}}{r_{12}}\,U(r_2)\,\phi(\underline{r}_2)\,d\tau_2 = \phi(\underline{r}_1).$$

It therefore appears that (3.67) has no solution and this is true if one is seeking an exact solution. However, to obtain β correctly in the limit as $d\to\infty$ it is only necessary to retain terms of order $e^{-\alpha_p d}$ and to this order the right hand side of (3.57) is orthogonal to $U(r_1)\,\phi\,(\underline{r}_1)$. It may be explicitly orthogonalized to $U(r_1)\,\phi\,(\underline{r}_1)$ by adding the term

$$-\frac{U(r_1)\,\phi(\underline{r}_1)}{4\pi}\sum_{s\neq 0} e^{i\underline{k}\cdot\underline{R}_s}\iint U(r_1)\,\phi(\underline{r}_1)\,\frac{e^{-dr_{12}}}{r_{12}}\,U(r_2)\,\phi(\underline{r}_2-\underline{R}_s)\,d\tau_2$$

which is of order $e^{-\alpha d}$ and therefore negligible. If this term

were added to the right hand side of (3.57) it would then be safe to attempt an exact solution, afterwards neglecting terms of lower order than the dominant ones. However, a much simpler approach is a variational one and all trouble is avoided by using trial functions which are orthogonal to $U(r_1)\,\phi\,(\underline{r}_1)$. It is first convenient to separate (3.57) into different spherical harmonic components.

Suppose

$$\sum_{s\neq 0} e^{i\underline{k}\cdot\underline{R}_s}\,\phi(\underline{r}-\underline{R}_s) = \sum_{l,m} g_{lm}(r)\,Y_{lm}(\theta,\phi)\,, \tag{3.59}$$

where (r, θ, ϕ) are spherical polar co-ordinates of $\underline{r}$, and

$$\beta(\underline{k},\underline{r}) = \sum_{l,m} f_{lm}(\underline{k},r)\,Y_{lm}(\theta,\phi)\,. \tag{3.60}$$

Also, using a well-known expansion [Mott and Sneddon (1948), p. 387] for $e^{-\alpha r_{12}}/r_{12}$ and the additional theorem for Legendre polynomials, one has

$$\frac{e^{-\alpha r_{12}}}{r_{12}} = \frac{4\pi}{(r_1 r_2)^{1/2}} \sum_{l,m} I_{l+\frac{1}{2}}(\alpha r_1)\,K_{l+\frac{1}{2}}(\alpha r_2)\,Y_{lm}(\theta_1,\phi_1)\,Y_{lm}(\theta_2,\phi_2)$$

for $r_1 < r_2$. In the case when r_1 may also be greater than r_2

it is convenient to write

$$\frac{e^{-\alpha r_{12}}}{r_{12}} = 4\pi \sum_{l,m} L_{lm}(r_1, r_2)\, Y_{lm}(\theta_1, \phi_1) Y_{lm}(\theta_2, \phi_2) \tag{3.61}$$

where

$$L_{lm} = (r_1 r_2)^{-\frac{1}{2}} \{ I_{l+\frac{1}{2}}(\alpha r_1) K_{l+\frac{1}{2}}(\alpha r_2)\, \Theta(r_2 - r_1) + I_{l+\frac{1}{2}}(\alpha r_2) K_{l+\frac{1}{2}}(\alpha r_1)\, \Theta(r_1 - r_2) \} \tag{3.62}$$

and

$$\Theta(x) = 1 \quad , \quad x > 0$$

$$0 \quad , \quad x < 0 \quad .$$

On substituting (3.59), (3.60) and (3.61) into (3.57), integrating over θ_2, ϕ_2 and equating coefficients of $Y_{lm}(\theta_1, \phi_1)$ one finds

$$U(r_1) \int_0^{r_d} L_{lm}(r_1, r_2)\, g_{lm}(k, r_2)\, r_2^2\, dr_2 + g_{lm}(k, r_1) = U(r_1) \int_0^{r_d} L_{lm}(r_1, r_2)\, U(r_2)\, g_{lm}(r_2)\, r_2^2\, dr_2 \tag{3.63}$$

This is an inhomogeneous Fredholm equation of the second kind and

it is not difficult to set up a variational principle for its solution. It must be remembered that for the equation with l, m corresponding to the angular symmetry of ϕ it is necessary to use a trial function for b_{lm} which is orthogonal to $U\phi$. Other components of β are automatically orthogonal to $U\phi$ and no restriction need be made on the trial function for these. The practicability of the method described here has been tested successfully with some calculations on an s-band in a simple cubic lattice of spherical square wells. In that case a few terms of a power series served as adequate trial functions; the example is not of sufficient intrinsic interest to justify giving lengthy details here. The complete solution for β correct to order $e^{-\alpha pd}$ is, from (3.55) and (3.60),

$$\beta(\underline{k},\underline{r}) = \sum_{l,m} b_{lm}(\underline{k},r) Y_{lm}(\theta,\phi) - [V-U(r)]\phi(\underline{r}). \tag{3.64}$$

The first term is zero for $r > qd$.

It has been shown that, in the case of a 'muffin-tin' potential for which the spherical non-zero potential regions do not touch, the problem of finding the asymptotically exact correction term to the tight-binding method reduces to the reasonably simple problem of solving (3.57). However, if the spheres of the 'muffin-tin'

potential touch, i.e. $q = \frac{1}{2}$, the step from (3.56) to (3.57) in which the exterior solution (3.55) is substituted for $\beta(\underline{k}, \underline{r}_2 - \underline{R}_s)$ does not give (3.57) correctly to order $e^{-\alpha pd}$. In fact the interior part of $\beta(\underline{k}, \underline{r}_2 - \underline{R}_s)$, i.e. that part with $|\underline{r}_2 - \underline{R}_s| < qd$, affects the interior part of $\beta(\underline{k}, \underline{r}_1)$ through the $e^{-\alpha r_{12}}/r_{12}$ term in (3.56). However, since $e^{-\alpha r_{12}}/r_{12}$ is of short range, this 'interaction' is only important near where the adjacent spheres touch. In this region β is small because U is small and it should be a reasonable approximation to neglect this 'interaction'. After solving (3.57) it might be possible to treat (3.56) more exactly, if necessary, by an iterative procedure.

It has been assumed for convenience in the above that $U_d(r) = v_d(r)$, [see equation (3.29)]. However a situation of common occurence is the case of a 'muffin-tin' potential with touching spheres and $U_d(r)$ chosen to be equal to $v(r)$, which only coincides with $v_d(r)$ for $r < qd$. The equation analogous to (3.45) and (3.54) is then

$$U_d(r_1) \int G(\underline{r}_1, \underline{r}_2)\, \beta(\underline{k}, \underline{r}_2)\, d\underline{r}_2 - \beta(\underline{k}, \underline{r}_1) = [V_d - U_d(r_1)]\, \phi(\underline{r}_1).$$

The suffix d has been kept here since it is necessary to distinguish between $v_d(r)$ which is zero for $r > qd$ and $v(r)$ which is not. Equation (3.55) holds and (3.57) becomes

$$\frac{v_d(r_1)}{4\pi}\int \frac{e^{-\alpha r_{12}}}{r_{12}}\beta(\underline{k},\underline{r}_2)\,d\tau_2 + \beta(\underline{k},\underline{r}_1)$$

$$= \frac{v_d(r_1)}{4\pi}\sum_{s\neq 0} e^{i\underline{k}\cdot\underline{R}_s}\int \frac{e^{-\alpha r_{12}}}{r_{12}}\left[v_d(r_2)-U_d(\underline{r}_2-\underline{R}_s)\right] \phi(\underline{r}_2-\underline{R}_s)\,d\tau_2.$$

It is necessary to make a spherical harmonic expansion of

$$\sum_{s\neq 0} \exp(i\underline{k}\cdot\underline{R}_s)\, U_d(\underline{r}-\underline{R}_s)\,\phi(\underline{r}-\underline{R}_s)$$

in addition to (3.59), and (3.65) gains an extra term. The treatment is unaltered, however, and the solution β is of the form (3.64) with $U(r) = v(r)$.

10.4 The corrected wave function and energy

The above procedure shows how to obtain β in the form (3.64) and this can now be substituted in expression (3.47) and (3.48) for the wavefunction and energy. Using (3.43) it is first of all possible to write (3.47) in the form

$$\psi(\underline{k},\underline{r}) = f(\underline{k},\underline{r}) + N^{-\frac{1}{2}}\sum_s e^{i\underline{k}\cdot\underline{R}_s}\,\xi(\underline{r}-\underline{R}_s) \qquad (3.65)$$

where

$$\xi(\underline{r}_1) = \frac{1}{4\pi} \int \frac{e^{-\alpha r_{12}}}{r_{12}} \beta(\underline{k}, \underline{r}_2) d\tau_2 \,. \tag{3.66}$$

On substituting for β from (3.64) and using (3.61) one finds

$$\xi(\underline{r}_1) = \sum_{l,m} Y_{lm}(\theta_1, \phi_1) \int_0^{qd} L_{lm}(r_1, r_2) f_{lm}(\underline{k}, r_2) r_2^2 dr_2 - \frac{1}{4\pi} \int \frac{e^{-\alpha r_{12}}}{r_{12}} [V - U(r_2)] \phi(\underline{r}_2) d\tau_2 \,. \tag{3.67}$$

The second term only affects the wave function appreciably in the outer regions of a unit cell and, as will be seen, makes a smaller contribution to the energy correction than does the first term. The first term is the more interesting and is a sum of localized functions of different angular symmetries. Each radial function falls off as $e^{-\alpha r_1}$, for $r_1 > qd$ because of the factor $K_{l+\frac{1}{2}}(\alpha r_1)$ in L_{lm}. Thus the correction to the tight-binding wave function in (3.65) is a sum of Bloch functions formed from localized functions of different angular symmetries. It is significant that each radial functions falls off as $e^{-\alpha r_1}$ which would not be the case if one

attempted to supplement the original Bloch function with a few Bloch functions formed from the more extended higher atomic orbitals. Practical difficulties in the latter approach have been noted (Parmenter 1952) and the present considerations make it clear that a large number of orbitals of each symmetry type would be required to build up the correct wave functions. The present method bypasses all these difficulties and also automatically includes corrections due to any non-orthogonality of the original Bloch function to the core functions. The contribution of a given angular term to the wave function is determined by the corresponding function b_{lm} which in turn is determined, through equation (3.63), by the function $g_{lm}(r)$ which appears in (3.59). It is therefore interesting to see that each angular term in the correction to the wave function is induced by the corresponding term in the expansion of the original Bloch function about the origin, the atomic function at the origin being omitted. This automatically ensures that for a given $\underline{k}$ only those angular terms contribute which are allowed by crystal symmetry. The above discussion has concentrated on the first term of (3.67) which is the more interesting and also the easier to calculate once β is known. However, the points made above require no modification if the second term is included, since for $r_1 > qd$ this also falls off as $e^{-\alpha r_1}$

and may be expanded in spherical harmonics. In this case each angular term is induced by the corresponding term in the expansion of $[V - U(r)]\,\phi(\underline{r})$ about the origin.

The corrected energy is obtained by substituting (3.64) into (3.48) and using (3.45). Thus also using (3.66) one obtains

$$E(\underline{k}) = E'(\underline{k}) + \sum_s e^{i\underline{k}\cdot\underline{R}_s} \int \xi(\underline{r}_1 - \underline{R}_s)[V - U(r_1)]\,\phi^*(\underline{r}_1)\,d\tau_1 \tag{3.68}$$

which as $d \to \infty$ may be written

$$E(\underline{k}) = E'(\underline{k}) + \int \xi(\underline{r}_1)[V - U(r_1)]\,\phi^*(\underline{r}_1)\,d\tau_1 + \sum_{s \neq 0} e^{i\underline{k}\cdot\underline{f}_s} \int \xi(\underline{r}_1)\,U(r_1)\,\phi^*(\underline{r}_1 + \underline{f}_s)\,d\tau_1 \tag{3.69}$$

where the summation is over nearest neighbour sites $\underline{f}_s$. Since $\xi(\underline{r}_1)$ and $\phi(\underline{r}_1)$ both fall off as $e^{-\alpha r_1}$ the first integral in (3.69) resembles a degenerated three-centre integral in which the two wave function centres coincide, and may be neglected as $d \longrightarrow \infty$. Similarly, when (3.67) is substituted in the summation term of (3.69), the terms arising from the second terms of (3.67) are negligible. Then using (3.59) and assuming a centre of symmetry one finds

$$E(\underline{k}) = E'(\underline{k}) + \sum_{l,m} \int_0^{\frac{1}{2}d} \int_0^{\frac{1}{2}d} L_{lm}(r_1, r_2)\,\rho_{lm}(\underline{k}, r_2)\,U(r_1)\,q^*_{lm}(r_1)\,r_1^2 r_2^2\,dr_1\,dr_2 .$$

The correction to the energy is therefore obtained as a sum of terms arising from different angular terms in the corrected wave function.

No application of this method to a problem of real interest, has yet been made. The crux of the method is the step from (3.36) to (3.37) where the eigenvalue problem is eliminated. It may be worthwhile to illustrate the method in the simple one-dimensional case of the chain of δ-functions considered in section 9, and to verify that the proper asymptotic correction to the tight-binding method is obtained.

11. Application to the δ-function Model

It is possible to follow through the solution of (3.45) for the one dimensional chain of δ-functions in a way quite analogous to the general method of section 10.3. In the notation of section 9 the one-dimensional equivalent of the Green function (3.42) is

$$G(x_1, x_2) = -\frac{1}{b} \sum_{n=-\infty}^{\infty} \frac{\exp\left[i y (k + 2\pi n/b)\right]}{(k + 2\pi n/b)^2 + \rho^2}$$

$$= -\frac{1}{2\rho} \sum_{m=-\infty}^{\infty} \exp\left\{-\rho |y - mb| + ikmb\right\} \qquad (3.70)$$

where $y = x_1 - x_2$. $G(x_1, x_2)$ may also be written in closed form for y in an interval (0, b) but the form (3.70), which is the analogue of (3.45), is in fact more convenient. Writing $E' = E_0 + \epsilon'$ to conform to the notation of section 9 and using (3.16), (3.17) and (3.18) one obtains the analogue of (3.45) in the form

$$-2\rho\,\delta(x_1)\int_{-\infty}^{\infty} G(0,x_2)\,\beta(k,x_2)\,dx_2 - \beta(k,x_1)$$

$$= \left[-\epsilon' - 2\rho \sum_{n\neq 0} \delta(x_1 - nb)\right] \sqrt{\rho}\, e^{-\rho|x_1|}. \tag{3.71}$$

It is required to solve this correct to order e^{-Pb}. For $x_1 > 0$,

$$\beta(k,x_1) = -\left[\epsilon' + 2\rho \sum_{n\neq 0} \delta(x_1 - nb)\right] \sqrt{\rho}\, e^{-\rho|x_1|} \tag{3.72}$$

and in this simple case $\beta = 0$ for $x_1 = 0$ [The right hand side of (3.71) may be taken as zero <u>at</u> $x_1 = 0$ in the step analogous to that from (3.41) to (3.45)]. The corrected wave function and energy may now be obtained by substituting (3.70) and (3.72) in the one-dimensional analogues of equations (3.47) and (3.48). One obtains [cf. (3.65)]

$$\psi(k,x) = f(k,x) + N^{-\frac{1}{2}} \sum e^{imkb}\, \xi(x - mb)$$

where

$$\xi(x) = \frac{\epsilon'}{2}\rho^{-\frac{1}{2}}\left(\frac{1}{\rho}e^{-\rho x} + x e^{-\rho x}\right) + \rho^{\frac{1}{2}} e^{-\rho b}\left(e^{-\rho|x+b|} + e^{-\rho|x-b|}\right)$$

and $f(k,x)$ is the original Bloch function.

Clearly $\phi(x) + \xi(x)$ is the Wannier function for the band, correct to order $e^{-\rho b}$. The wave function may be written as

$$\psi(k,x) = f(k,x) - \left[2\rho^{3/2} e^{-\rho b}\cos kb\right] N^{-\frac{1}{2}} \sum_m e^{imkb}\,|x-mb|\,e^{-\rho|x-mb|}$$

and the correction to the wave function is thus a Bloch sum formed from a localized function $|x|\exp(-\rho|x|)$. An equation similar to (5.68) gives the correction to the tight-binding energy expression in the form

$$2\rho^2 e^{-\rho b}\cos kb \sum_m e^{imkb} \int |x-mb|\, e^{-\rho|x-mb|} \left[\epsilon' + 2\rho \sum_{n\neq 0} \delta(x-nb)\right] e^{-\rho|x|}\, dx$$

Only the ϵ' term in square brackets contributes to order e^{-2Pb} and the energy correction is easily shown to equal the proper expression (3.28). This forms a check of the method.

CHAPTER 4

THE VALIDITY OF THE TIGHT-BINDING METHOD FOR D BANDS IN THE TRANSITION METALS

The aim of this chapter is to apply the ideas of Chapter 3 to the case of d bands. The method of section 8.1 is used to estimate upper bounds to the errors expected in a tight-binding calculation and the question of the best choice of 'atomic' potential is considered. The conclusions reached are summarized in section 13.

12. Errors and the best choice of 'atomic' potential to avoid them

12.1 Estimate of the error in a typical calculation

In this section it is proposed to estimate the error incurred in a typical tight-binding calculation of d bands when only Bloch functions formed from 3d orbitals are used. This estimate will be based on Fletcher's (1952) calculation for Ni. It was first pointed out in section 7 that the crystal potential used by Fletcher was not clearly defined and it will be replaced here by a 'muffin-tin' potential of the form (2.1) with

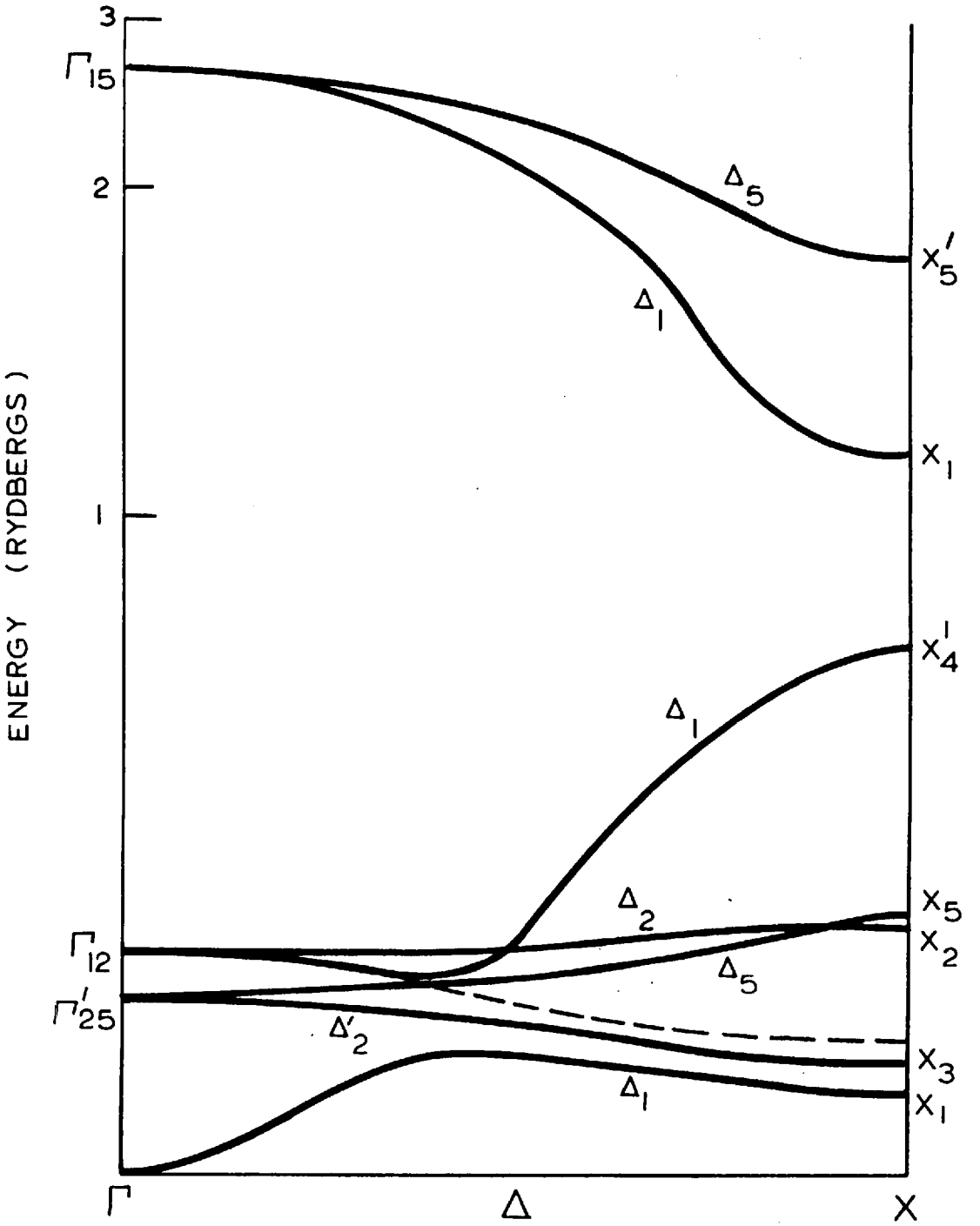

FIGURE 4: Schematic diagram of bands along the Δ axis.

$$v(r) = U_f(r) - U_f(r_o) \quad , \quad r < r_o$$

$$0 \quad , \quad r > r_o \qquad (4.1)$$

where $U_f(r)$ is the 'atomic' potential used by Fletcher and r_o is half the nearest neighbour distance, (d/2 in a previous notation). The 'atomic' potential here will be taken as

$$U(r) = U_f(r) - U_f(r_o) \qquad (4.2)$$

for all r, which differs from Fletcher's only by a constant. It is unlikely that the band structure calculated for the 'muffin-tin' potential described would differ too much from that calculated by Fletcher. This is shown schematically in figure 4 for the (001) direction and the full lines show the type of structure to be expected when other bands are included. Fletcher made the two-centre nearest neighbour approximation but this could have been avoided with some effort. In fact the error made through this approximation is probably not very large. The concern of this section is the error made by only using the five Bloch functions formed from 3d atomic functions, and for simplicity states along the Δ axis are mainly considered. Along this axis the Bloch functions formed from different d functions do not mix and it follows from section 8.2 that an upper bound to the error for a typical

state in the band associated with the atomic function ϕ_n is

$$|\Delta E_{min}|^{-1} \int |\phi_n(\underline{r})|^2 \left[V - U(r)\right]^2 d\tau. \tag{4.3}$$

ΔE_{min} is the energy interval between the tight-binding approximation to the state considered and the exact energy of the nearest neighbouring state of the same symmetry. It is clear from figure 4 that apart from states of Δ_1 and X_1 symmetry it is safe to insert a value of 2.5 rydbergs for ΔE_{min}. (The nearest core level is about 5 rydbergs down). The integral in (4.3) will now be evaluated using methods described in section 17.3.

Using (2.1) one may write the integral as

$$\begin{aligned} \int |\phi_n(\underline{r})|^2 \left[V - U(r)\right]^2 d\tau \\ = \sum_{s \neq 0} \int |\phi_n(\underline{r})|^2 \left[v(\underline{r} - \underline{R}_s)\right]^2 d\tau \\ - 2 \sum_{s \neq 0} \int |\phi_n(\underline{r})|^2 U(r)\, v(\underline{r} - \underline{R}_s)\, d\tau \\ + \int_{r > r_0} |\phi_n(\underline{r})|^2 \left[U(r)\right]^2 d\tau . \end{aligned} \tag{4.4}$$

It turns out that the last two terms are considerably smaller than the first so attention will be concentrated on this one. Only nearest neighbour sites need be included in the sum. Following a method described later in section 17.2 one may express the integral

$$I_s^{(n)} = \int |\phi_n(\underline{r})|^2 \left[v(\underline{r} - \underline{R}_s)\right]^2 d\tau$$

in terms of integrals which involved d functions referred to new axes Ox'y'z' where Oz' is in the direction of $\underline{R}_s$. The original d functions $\phi_n(\underline{r})$ are given by (5.6) referred to the cubic axes of the crystal and the transformed d functions $\phi_{n'}(\underline{r})$ are given by similar expressions but with primed co-ordinates. With new integrals defined by

$$I^{(n')} = \int |\phi_{n'}(\underline{r})|^2 \, [v(\underline{r} - \underline{R}_s)]^2 \, d\tau \tag{4.5}$$

it is found, as in section 17.2, that

$$\sum_{s \neq 0} \int |\phi_n(\underline{r})|^2 \, [v(\underline{r} - \underline{R}_s)]^2 \, d\tau$$

$$= 5I^{(1')} + 4I^{(2')} + 3I^{(5')} \quad , n = 1, 2, 3$$

$$\frac{9}{2} I^{(1')} + 6I^{(2')} + \frac{3}{2} I^{(5')} \quad , n = 4, 5 \tag{4.6}$$

The d functions occurring in $I^{(1')}$ and $I^{(2')}$ have nodes passing through the potential centre and $I^{(5')}$ makes much the largest contribution to these expressions. It follows from the above discussion that, apart from states of Δ_1 and X_1 symmetry, a typical error in rydbergs should not be larger than the numerical value of $I^{(5')}$ in $(\text{rydbergs})^2$. A more accurate calculation which included the second term in (3.10) would lead to lower upper bounds to the error for some states, but higher upper bounds for others. No error should be greater than twice the typical one indicated and

the error in the X_1 state should also not be worse than this. $I^{(5')}$ may be calculated by the method indicated in section 17.2 and it is found to be 0.04 (rydbergs)^2 to a good approximation. The radial wave function used was Fletcher's analytic approximation to the Hartree-Fock function. It is interesting to note that, although $|\phi(r)|^2$ falls off very rapidly radially, the largest contribution to the integral comes from the immediate vicinity of the potential site because of the r^{-2} singularity in v^2. It is concluded that a typical error in the calculation should not be greater than 0.04 rydbergs for any state which does not interact with the overlapping sp band. This accuracy is sufficient to ensure that the ordering of levels at points of high symmetry is correctly given and shows that the tight-binding method is at least semi-quantitative. The accuracy may be considerably better than the upper bound estimate.

The above calculation possibly represents the tight-binding approximation in rather too favourable a light. Fletcher employed Hartree-Fock Cu^+ 3d functions and these correspond to a more attractive potential than exists in metallic Ni. These functions are more localized than they should be and this accounts for Fletcher's rather small band-width. It is clear from (4.3) that the accuracy of a tight-binding calculation depends largely on the degree of localisation of the atomic functions used. An example at the opposite extreme is to be found in Chapter 5. In the calculation on Cu reported

there very diffuse 'atomic' functions are used and by actual calculation the error in the tight-binding energies is found to be several times the true band width. 'Atomic' functions are determined from an 'atomic' potential which is usually closely related to the crystal potential. A tight-binding calculation can only be successful for a given metal if a reasonable choice of 'atomic' potential can be made such that the 'atomic' functions are sufficiently localized. The question of whether this is the case for copper and the transition metals is discussed in the next section.

12.2 Potentials

In the free atom of a transition metal a number of different configurations $(3d)^m(4s)^n$ have energies very close to each other. In the metal these configurations interact, the 4s band overlaps the 3d band, and it is unreasonable to use a potential corresponding to the lowest atomic configuration in the vicinity of each atom. This has been shown explicitly for body-centred cubic iron by Callaway (1955) and Stern (1955). Both these workers used a potential based on the self-consistent field for the $3d^6 4s^2$ configuration of atomic iron and in both cases the 3d band was found to lie completely below the 4s band. This would imply that the configuration in the solid was $3d^8$ which is inconsistent with the initial configuration assumed. Both calculations also found the band to be about 0.1 ry. wide, which is narrower than the width suggested by X-ray emission measurements

(Skinner, Bullen and Johnston 1954). Callaway's calculation was by the OPW method and Stern's by his modified tight-binding method. In Stern's case the narrowness of the band is due to the localized nature of the atomic functions and the situation is such that the tight-binding method is probably very accurate for the crystal potential used. Unfortunately the potential is not physically reasonable. Later calculations by Stern (1959) and Wood (1962) have shown that a potential based on a $3d^7 4s$ configuration leads to more reasonable results. Hanus (1960-62) has investigated the effects of different crystal potentials in Ni using the APW method. His initial calculation employed a potential based on a $3d^8 4s^2$ configuration and the s band was found to lie very low relative to the d band. The s band could accommodate two electrons below the d band which does not agree with the normal model of Ni with 0.6 s electrons. The d band width was 0.63 ry. Hanus also tried a potential based on a $(3d)^{10}$ configuration where the situation was found to be worse with a band width of 1.35 ry. This was only to be expected since a d electron is not bound so tightly if there are 9 other d electrons to screen the core. More recently Hanus has applied a suitable exchange potential correction to his original potential and finds that the d band lies in the middle of the first band of the sp bands and has a width of 0.33 ry.

The above discussion shows that choosing a suitable crystal

potential is not easy. The method at present is essentially one of trial and error until a potential is found which leads to a band structure consistent with known physical data. It is often remarked in the literature that modern computing techniques will soon make it possible to calculate self-consistent potentials. It was pointed out in section 2, however, that the difficulties of the many body problem are such that it is by no means clear what self-consistent problem has to be solved.

The question to be considered now is whether various crystal potentials, which have been found physically reasonable for transition metals, are suitable for a tight-binding approach. Crystal potentials of cellular or 'muffin-tin' form normally employ an atomic-like potential within the cell, or inscribed sphere, and the potential extrapolates smoothly to the form -2/r. This extrapolated potential is the most natural choice of 'atomic' potential for a tight-binding calculation and the suitability of this choice will presently be considered for several crystal potentials for which band calculations exist. In a tight-binding calculation of d bands the bands spread to an almost equal extent above and below the eigenvalue E_0 of the 'atomic' function, calculated in the 'atomic' potential. Thus by examining a band structure, which has been calculated by some method for a given crystal potential, it is possible to infer the binding energy of the natural choice of 'atomic' function.

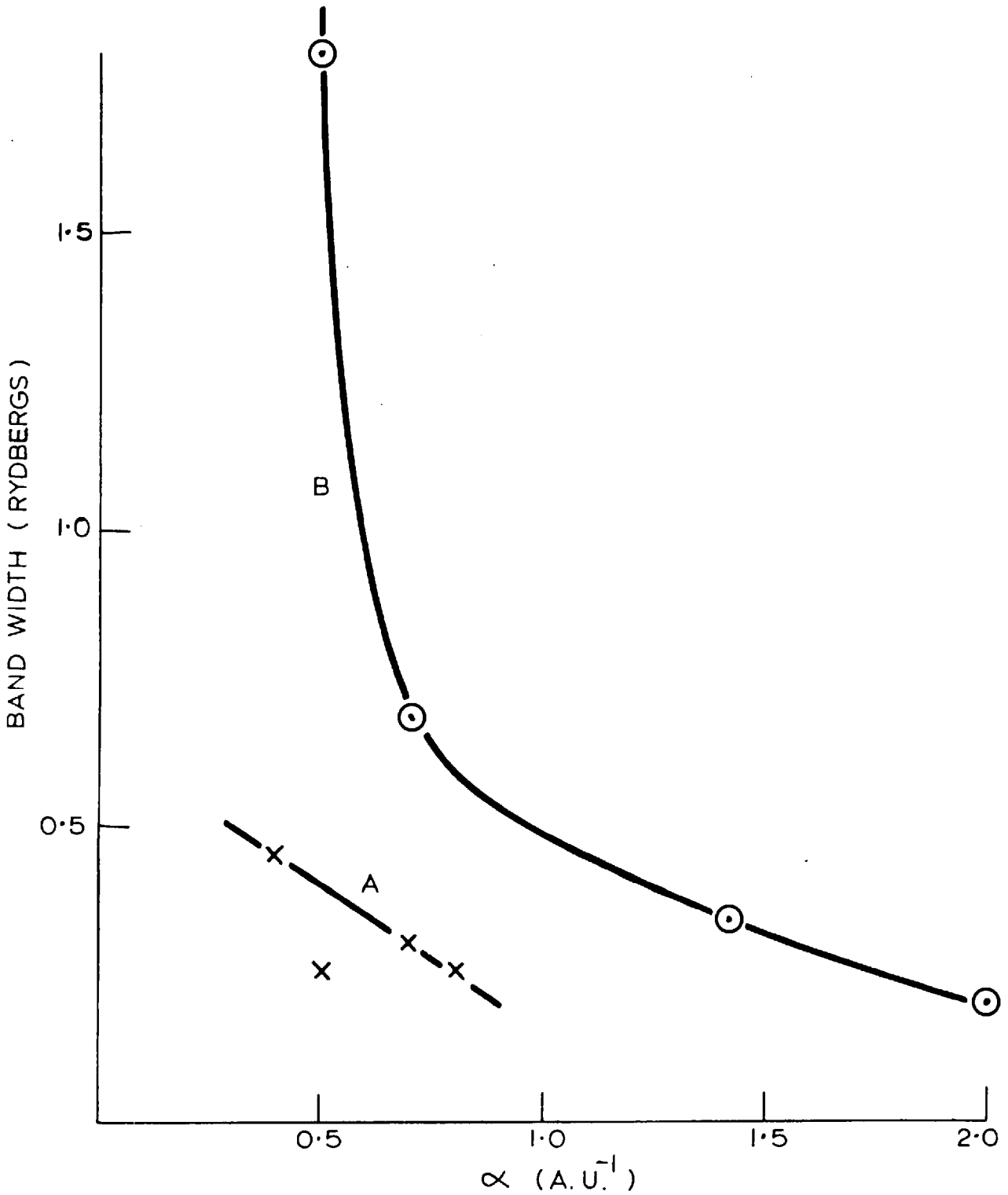

FIGURE **5**: Graphical plot of the data in tables A and B.

This binding energy determines the localization of the 'atomic' function which for large r varies as $r^2 e^{-\alpha r}$ where $\alpha^2 = -E_0$. It is then possible to decide on the suitability of the tight-binding method. Values are listed in table A of α estimated in this way from various band structures calculated accurately by methods other than tight-binding. The width of the d band is also indicated. The results of Manus (1962) on Mi are not given since his potential does not extrapolate to -2/r and the natural choice of 'atomic' potential indicated above is not possible. From table A it is seen, as would be expected, that the band width is smaller when the d bands lie lower, i.e. when the 'atomic' function is more localized. From this point of view Howarth's band width is unexpectedly small or, alternatively, his d band lies unexpectedly high. To discover whether a tight-binding calculation based on the natural 'atomic' functions would lead to reasonable results in the above situations, it is necessary to examine the band-widths obtained using 'atomic' functions with various degrees of localization. Values of α and band width for some existing tight-binding calculations are given in table B.

The data of tables A and B are represented graphically in figure 5. It is clear that tight-binding calculations for the crystal potentials of table A calculations, and with a natural choice of 'atomic' potentials, would inevitably lead to band widths considerably larger than the true ones. For example a tight-binding calculation

TABLE A

			α (A.U.$^{-1}$)	Band width (ev.)
Howarth	(1953)	Cu	0.5	0.26
Segall	(1962)	Cu (1st potential)	0.8	0.26
		Cu (2nd potential)	0.7	0.30
Wood	(1962)	F.C.C. Fe	0.4	0.45
		B.C.C. Fe	0.4	0.46

TABLE B

			α (A.U.$^{-1}$)	Band width (ev.)
Fletcher	(1953)	Ni	2.0	0.2
Belding	(1959)	B.C.C. Fe	1.42	0.34
Stern	(1959)	B.C.C. Fe	0.7	0.68
Edwards (see Chap.5)		Cu	0.5	1.80

for Cu using Segall's second potential, and using a natural choice of 'atomic' potential, would almost certainly lead to a band width nearer Stern's value of 0.68 ry. than the accurately calculated one of 0.30 ry. This inference can be made, in spite of the fact that Stern's calculation is for B.C.C.Fe, because, in the region of $\alpha < 1$, band widths in a tight-binding calculation are more sensitive to changes in 'atomic' function than to changes in crystal potential and structure. This of course assumes that differences in crystal potential are not large and that the nearest neighbour distance is not changed much. These conditions obtain in the present case. For the case of Howarth's Cu potential a tight-binding calculation with a natural choice of 'atomic' potential is reported in Chapter 5. The band width is found to be much too large. This result is not surprising since it is pointed out in section 18 that an upper bound to a typical error, calculated from (4.4), is about 2 rydbergs in this case.

The evidence cited above shows clearly that a natural choice of 'atomic' potential must be abandoned in calculating d bands. Reasonable results are only obtained if $\alpha > 1$ and to ensure this the binding energy of the 'atomic' function in the 'atomic' potential must be greater than 1 rydberg. Some obvious alternative choices of 'atomic' potential are shown in figure 6. The broken lines show the modified 'atomic' potentials and the full lines show the natural choice

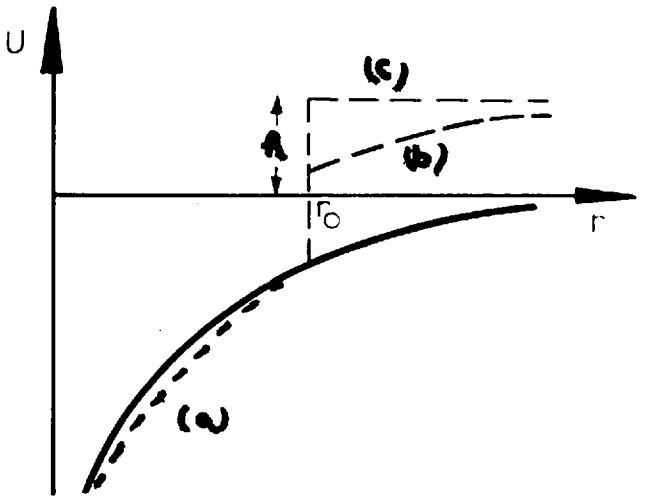

Fig. 6

of atomic potential. In case (a) the potential is generally deepened, particularly in the region where the radial d function peaks. In cases (b) and (c) a step is introduced into the 'atomic' potential on the 'muffin-tin' sphere. The relative merits of these possibilities may be studied using the criterion indicated in section 8.2. The 'atomic' potential U should be chosen so that the integral

$$\int |\phi(\underline{r})|^2 \left[E_0 - E' + V - U\right]^2 d\tau \qquad (4.7)$$

is as small as possible. $\phi(\underline{r})$ is an eigenfunction for the potential U with eigenvalue E_0 and E' is a typical energy in the band calculated by the tight-binding method. E' may be taken as the 3d eigenvalue in the natural choice of 'atomic' potential. $E_0 - E'$ is not neglected

as has been done previously, since it is not negligible in case (a) where there is a large energy shift ($\sim$ 1 rydberg). To achieve approximately the same α for the 'atomic' function in all cases the potential step h must be equal to the energy difference $E' - E_0$ in case (a). It is then clear that the contribution to the integral (4.7) from the region $r > r_0$ is of similar magnitude in all cases. In case (a), however, there is a contribution from $r < r_0$ which may be quite large, although the large $E' - E_0$ term must approximately cancel V - U over part of the range. The best choice of 'atomic' potential thus appears to be one of type (b) or (c).

It is simple to estimate an upper bound to the error in a typical tight-binding calculation in which 'atomic' functions as localized as the Hartree-Fock Cu^+ 3d functions are obtained by using an 'atomic' potential of type (c). It is only necessary to recalculate expression (4.4) with U taking a constant value of $(h + 3/r_0)$ rydbergs. If this is done with h = 1 it is found that the ~~best~~ last two terms are no longer negligible and the value of (4.4) is approximately twice that calculated in section 12.1. Thus a typical error in the calculation should not be greater than 0.08 rydbergs for any state which does not interact with the overlapping sp band. If the same 'atomic' functions were obtained using a potential of type (b) the upper

bound estimate would be smaller, perhaps about 0.06 rydbergs. It is probable that the accuracy is well within the bounds set. Thus if an 'atomic' potential of type (b) is used the tight-binding method cannot lead to any of the wild inaccuracies which can occur when the natural choice of 'atomic' potential is made for d bands. Ideally the actual potential step introduced should be chosen so as to minimise (4.7). Fortunately however the band structure obtained will be fairly insensitive to the exact value of α, and hence of h, for the following reasons. Firstly it is seen from figure 5 that the band width only decreases relatively slowly as α increases for $\alpha > 1$. Secondly as h, and hence α, increases the magnitude of the factor $V - U$ in the energy integrals increases. These two effects tend to compensate.

It might appear that by introducing a potential step into the 'atomic' potential, and thus obtaining very localized 'atomic' functions, a tight-binding viewpoint has been artificially imposed on the system. This is not so however since the potential step device only works when the charge distribution corresponding to the natural choice of 'atomic' function is such that most of the charge lies within the sphere inscribed in the unit cell. When the natural 'atomic' function is more diffuse, e.g. conduction electrons in Na, the effect of a potential step is merely to force up the energy without greatly increasing the binding. Thus, even using the potential

step device, the tight-binding approximation can only be used for electrons which are quite tightly bound. Further evidence for the appropriateness of the tight-binding method for d bands is the simple 'tight-binding-like' form of E(k) curves obtained in accurate calculations by Wood (1963) for Fe and Segall (1958) for Cu. Cornwell and Wohlfarth (1961) were able to fit Wood's results very well using tight-binding interpolation formulae.

The great drawback to the usual tight-binding method for d bands is that it does not deal with the s and p bands which overlap the d band. These bands and their interactions with the d band cannot be treated by the usual tight-binding method since the 4s and 4p atomic functions have large overlaps with neighbouring atoms. In the next section it is considered whether the ideas of Chapter 3 can be used to provide corrections to the tight-binding method and to deal with the problem of sp overlap.

11.5 The problem of sp overlap

It is first of all worth considering whether the asymptotic correction method of section 10 can be used to calculate corrections to the tight-binding method in the case of d bands. Unfortunately this is not the case since the method can only be applied when the 'atomic' functions are actually bound in the 'muffin-tin' well, i.e. when the eigenvalue for the 'atomic' function lies below the constant of potential between spheres. This is not the case for d bands when realistic crystal potentials are used. The asymptotic correction

method could probably be applied successfully to Stern's (1955) initial tight-binding calculation for Fe in which the d band lay completely below the s band. Realistic d bands lie just within the range of applicability of the tight-binding approximation, although care is needed as was discussed in section 10.3, but outside the range of applicability of the asymptotic correction method.

The problem of how to deal with the overlapping s and p bands in a tight-binding calculation remains an unsolved one. One tentative suggestion may be made here. In section 10.4 it was pointed out that corrections to the tight-binding wave function take the form of Bloch sums

$$\sum_s \exp(i\underline{k}\cdot\underline{R}_s)\, \zeta(\underline{r} - \underline{R}_s)$$

where ζ is the product of a spherical harmonic and a radial function which falls off exponentially as rapidly as the tight-binding 'atomic' function. In the case of d bands, although the asymptotic correction method does not apply, it is nevertheless worth considering the use of similar functions. One could construct 4s and 4p functions which resemble the corresponding atomic functions over the core region, so that they are orthogonal to the core functions, but which fall off exponentially as fast as the d 'atomic' functions. Bloch sums formed from these could be used, together with the d functions, to set up

the usual secular equation. The matrix elements could be easily calculated because all the atomic functions used would be quite localized. It may be significant that accurate calculations (Wood 1962, Segall, 1962) show that the sp band is closer to a tight-binding form of band than to free electron bands. The band gaps at the zone boundaries are large. Cornwell and Wohlfarth (1961) were able to fit Wood's sp and d bands with tight-binding formulae. It may also be significant that Mollner (1959) was able to fit Pippard's (1957) Cu Fermi surface with terms of tight-binding form. [See also a reference to D.J. Roaf in the paper by Segall (1962)].

15. Conclusions

The stimulus for the work described in this chapter and the preceding one was the rather unsuccessful calculation which is reported in Chapter 5. A possible sequel to this initial calculation which failed through making the natural choice of 'atomic' functions, would have been to repeat the calculation with more localized, and rather arbitrarily chosen, 'atomic' functions. A more reasonable set of E(k) curves would certainly have been obtained but it was felt that little would be gained by adding to the existing number of such arbitrary calculations, of unknown accuracy. A more fundamental examination of the basis of the tight-binding method was therefore undertaken and the

main conclusions will be summarized here. It is felt that the way has now been prepared for better understood and more carefully controlled applications of the tight-binding method, particularly to the study of d bands.

The main conclusions are as follows.

(1) The 'atomic' functions in a tight-binding calculation must be well localized.

The error in the calculation due to using a restricted set of trial functions is likely to be large unless the nearest neighbour approximation is a good one. It will rarely be worthwhile pursuing a tight-binding calculation beyond second nearest neighbour integrals. This conclusion was reached by general arguments in section 8, and in section 9 the error in the tight-binding method was calculated explicitly for a chain of δ-functions. The calculation reported in the next chapter shows how large errors arise if the 'atomic' functions are insufficiently localized.

(2) The 'muffin-tin' potential is the most suitable form of crystal potential for a tight-binding calculation. The reasons for this are the following:

(a) Accuracy. Accurate results for a given crystal potential are most likely to be obtained if the 'atomic' functions correspond to an 'atomic' potential which coincides with

the crystal potential within the sphere inscribed in the unit cell. This condition cannot be satisfied if the crystal potential is constructed from overlapping potentials. A cellular type of potential has practical disadvantages but the 'muffin-tin' potential is ideal. With the 'atomic' functions chosen as indicated the trial Bloch functions are nearly orthogonal to the core functions. Non-orthogonality to the core only arises from overlap of the 'atomic' functions with core functions on neighbouring sites, and this must be negligible if condition (1) above is satisfied.

(b) Practical advantages. It was pointed out in section 6.3 that with a 'muffin-tin' potential the sum of three-centre integrals in (9.24) is rapidly convergent. If condition (1) is well satisfied three-centre integrals are a minor correction to the two-centre approximation and may easily be calculated since the integrations are over spheres. A method to be described in section 17.3 is a convenient means of calculating them.

(c) The availability of a correction method. In section 10 a method was developed for correcting the tight-binding method for the error which arises through using a restricted set of trial functions. The method applies when the crystal potential is of 'muffin-tin' form and when the 'atomic' functions

correspond to states bound in the 'muffin-tin' well. In section 11 the method was applied to the simple δ-function model. In the general case it is interesting to see how corrections of different angular symmetries are generated by terms of these symmetries which exist in the original trial functions when expanded about a lattice site.

(3) Reasonable accuracy can be attained in a tight-binding calculation of d bands, at least for those states which do not interact with the overlapping sp band, provided the correct choice of 'atomic' potential is made.

A natural choice of 'atomic' potential is obtained by extrapolating the potential within the 'muffin-tin' sphere to a coulombic form for large r. In this chapter it was shown that this choice of 'atomic' potential is a very poor one for d bands. In order to produce sufficiently localized 'atomic' functions it is necessary to introduce into the 'atomic' potential a potential step of about 1 rydberg on the 'muffin-tin' sphere. This is preferable to using an 'atomic' potential which is deepened within the sphere; the latter method leads to results of uncertain accuracy. It has been argued that the band structure should be insensitive to the exact potential step introduced and a criterion for choosing a reasonable one has been given. The use of more localised functions makes the calculation simpler and more accurate at the same

time. The nearest neighbour approximation may be a good one, although in a good calculation the next nearest neighbour two-centre integrals and the largest three-centre and non-orthogonality integrals should be calculated. An upper bound to the error in a typical d band calculation, for a state which does not interact with the overlapping sp bands, is estimated to be about 0.06 ry. There are indications (see section 10) that in many cases the error may be very much smaller than the upper bound estimate. The problem of sp overlap is a difficult one but a suggestion for dealing with it has been made.

It is obvious that the tight-binding method cannot aspire to the accuracy which may be achieved by some other methods at a restricted number of points in the zone. Nevertheless the tight-binding method can give a reasonably accurate picture of energies and wave functions throughout the zone; it is convenient for calculating density of states curves and the wave functions are sufficiently simple to form a basis for physical theories.

CHAPTER 5

A TIGHT-BINDING CALCULATION FOR THE D BAND IN COPPER

In this chapter a calculation is described which was carried out to investigate directly, in a particular case, whether the structure of the d band may be obtained with reasonable accuracy by the tight-binding method using only the Bloch functions formed from the 3d 'atomic' functions. In the event the calculations give very poor results and the reason for the failure of the tight-binding method is obvious a posteriori. It appears that, through taking the natural choice of 'atomic' potential, the 'atomic' functions used were insufficiently localized. Nevertheless the calculation is reported here since, despite the negative result, it has some positive aspects and two of these may be mentioned now.

In section 16 a general method is described of reducing all the energy integrals to the smallest number of independent integrals. The procedure given is more convenient and systematic than that used previously by Slater and Koster (1954). A second feature of the calculation is a new method of calculating three-centre integrals which, to a fair approximation, reduces them to two-centre integrals; this is described in section 17.3. These features of the calculation made it possible to include a large number of three-centre integrals,

as well as two-centre and non-orthogonality integrals. Such a complete tight-binding calculation does not appear to have been done previously for a three-dimensional lattice although Corbato (1956) has carried out an extended calculation in the two-dimensional case of graphite.

14. Formulation of the Problem

The general discussion of Chapter 2 shows that to formulate a tight-binding calculation attention must be paid to the crystal potential $V(\underline{r})$ and the 'atomic' potential $U(r)$.

14.1 The crystal potential

Since the calculation is aimed at investigating the accuracy of the tight-binding method it is desirable to use a crystal potential for which some accurate eigenvalues are known. The tight-binding results may then be compared with the known values. At the time when the calculation was started the only existing accurate calculations on the d band in copper were the two calculations of Howarth. The first of these (Howarth 1953) was by the cellular method and the second (Howarth 1955) by the APW method.

The potential used in the cellular method is of the form $\sum v(\underline{r} - \underline{R}_i)$ where $v(\underline{r})$ is non-zero and spherically symmetric inside the unit cell containing the origin but zero outside this

cell. The integrals involved in a tight-binding calculation for this crystal potential would be integrals over unit cells, and extremely difficult to evaluate. The crystal potential used in the APW method is the "muffin-tin" potential which is spherically symmetric inside a sphere radius r_o surrounding each atom and constant between these spheres. The radius r_o is chosen so that the spheres just touch and the constant between spheres is chosen so that the potential is continuous across the boundaries of the sphere. Since the potential is arbitrary to the extent of an additive constant the constant value between spheres may be taken as zero. The potential is then of the form

$$V(\underline{r}) = \sum_i v(\underline{r} - \underline{R}_i) \qquad (5.1)$$

where $v(\underline{r})$ is spherically symmetric within the sphere, radius r_o, surrounding the origin and zero outside. It has been pointed out that such a potential is extremely suitable for a tight-binding calculation. It was therefore decided to use the same crystal potential as Howarth used in his APW calculation, and the results obtained in a tight-binding calculation should then be comparable with Howarth's. Although Howarth calculated the eigenvalues only at certain symmetry points in $\underline{k}$-space, the values at these points were claimed to be accurate. More recently, however, doubt has been thrown on the correctness of Howarth's calculation; this was discussed in section 4.

The crystal potential used by Howarth and used in the present

calculation, was formed to represent the $(3d)^9(4s)$ configuration. The function v(r) was obtained from the Hartree Cu^+ potential (Hartree 1933, 1934) as follows. A potential $v_c(r)$ was first formed by adding to the Hartree potential the contributions of an atomic 4s wave function in this field, normalized to unity inside the atomic sphere,* and subtracting the spherical average of the contribution from one atomic 3d wave function, also normalized to unity inside the atomic sphere. $v_c(r)$ was the potential used by Howarth in his cellular calculation. v(r) is now defined by

$$v(r) = v_c(r) - v_c(r_o) \quad , \quad r \leq r_o \qquad (5.2)$$
$$v(r) = 0 \quad , \quad r > r_o \ .$$

v (r) is tabulated in table 1. r_o = 2.41 atomic units for Cu and $v_c(r_o)$ = -0.9307 ry.

14.2 The 'atomic' potential

The natural choice of 'atomic' potential U(r) was made so that

$$U(r) = v_c(r) - v_c(r_o) \qquad (5.3)$$

for all r. Thus U(r) is equal to v(r) defined by (5.2) for $r < r_o$ but does not flatten off to zero for $r > r_o$. $v_c(r)$ extrapolates smoothly to - 2/r for large r. U(r) and v(r) are drawn schematically in figure 7.

A convenient analytic fit for U(r) for $r < r_o$, which will be designated $U_1(r)$ and was used in evaluating certain integrals, is the

* N.B. The sphere whose volume is the volume/atom in the metal.

following:

$$r^2U_1(r) = 40r - 50r^2 \quad , \quad 0 < r < 0.4 \qquad (5.4)$$
$$9.5 - 4r \quad , \quad 0.4 < r < 2.41$$

~~This is compared with the exact curve in figure.~~

For $r > 3.5$ $U(r)$ is given by

$$U_2(r) = 0.9307 - 2/r \qquad (5.5)$$

to an accuracy of 1%.

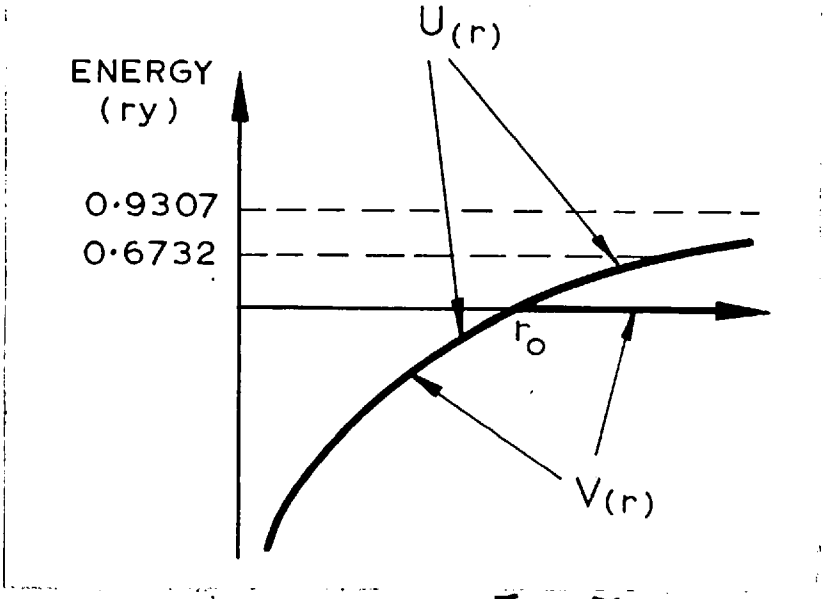

Fig. 7

14.3 The 'atomic' functions

The 'atomic' functions $\phi_i(\underline{r})$ to be used for constructing Bloch functions are the five degenerate wave functions of the 3d states bound by the potential $U(r)$. Thus referred to the cubic axes Oxyz

of the crystal

$$\phi_1 = \sqrt{\frac{15}{4\pi}}\ \frac{xy}{r^2} f(r)\ ,\quad \phi_2 = \sqrt{\frac{15}{4\pi}}\ \frac{yz}{r^2} f(r)\ ,\ \phi_3 = \sqrt{\frac{15}{4\pi}}\ \frac{zx}{r^2} f(r)$$

$$\phi_4 = \sqrt{\frac{15}{16\pi}}\ \frac{x^2-y^2}{r^2} f(r)\ ,\ \phi_5 = \sqrt{\frac{5}{16\pi}}\ \frac{3z^2-r^2}{r^2} f(r)\ ,$$

(5.6)

and

$$f(r) = \frac{1}{r} P(r)\ , \tag{5.7}$$

where $P(r)$ satisfies the equation

$$\frac{d^2P}{dr^2} = \left[\frac{6}{r^2} + U(r) - E_o\right]P \tag{5.8}$$

and is such that $f(r)$ is finite at the origin and tends to zero as $r \to \infty$. The eigenvalue E_H and the corresponding function $P_H(r)$ for the Hartree Cu^+ potential $U_H(r)$ are known (Hartree 1933) and these may be used in a first-order perturbation calculation to obtain a first approximation to E_o. Thus

$$E_o \simeq E_H + \frac{\int_0^\infty [P_H(r)]^2 (U - U_H)\,dr}{\int_0^\infty [P_H(r)]^2\,dr} \tag{5.9}$$

and the value given by Hartree for E_H is -1.195 ry.

With U defined by (5.3)

$$E_o \simeq -1.195 - v_c(r_o) + \frac{\int_0^\infty [P_H(r)]^2 (U - U_H)\,dr}{\int_0^\infty [P_H(r)]^2\,dr}$$

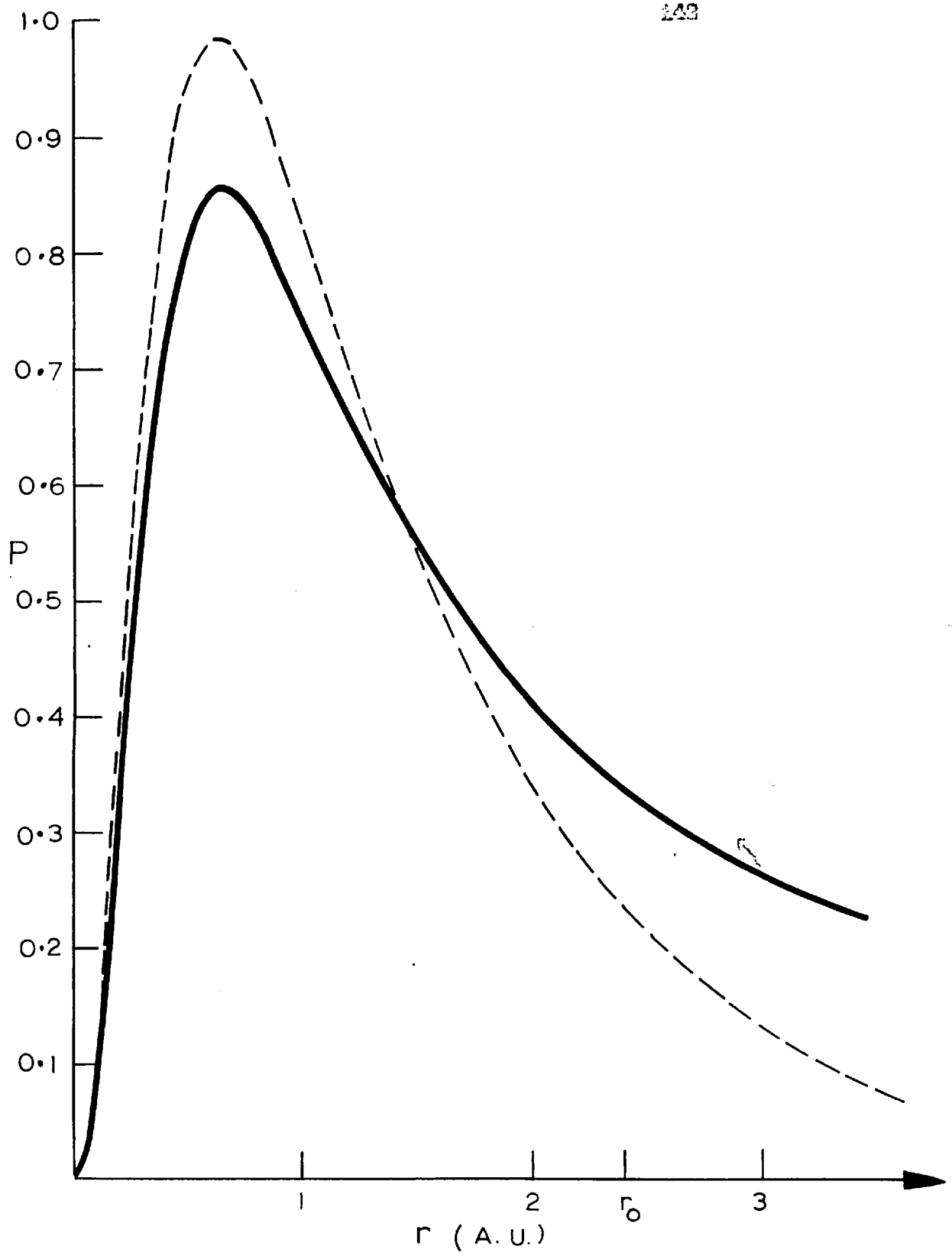

FIGURE 8 : Radial 'atomic' function calculated in Howarth's potential (full curve) compared with Hartree-Fock Cu^+ 3d function (broken curve)

and numerical integration leads to a value 0.70 ry for E_o. This served as a useful starting point for an accurate calculation of E_o and the corresponding function P. This calculation was carried out using methods described by Hartree (1928) and it was found that

$$E_o = 0.6732 \text{ ry}. \tag{5.10}$$

A graph of the corresponding function P is given in figure 8 where it is compared with the Hartree-Fock Cu^+ function used by Fletcher (1952). The latter function falls off much more rapidly as r increases and this, of course, is due to the more attractive potential in the ion.

It can now be pointed out that the second choice of U(r) which might be considered, viz. U(r) = v(r) for all r, is in fact not possible. This is because if an approximate E_o is calculated from (5.7) with U(r) = v(r) a value not much different from (5.8) is obtained. This is positive and thus the potential well v(r) has no bound 3d state. It will be seen from figure 7 that the binding energy of the 3d state in the potential of U(r) is

$$0.9307 - 0.6732 = 0.2575 \text{ ry}$$

14.4 Analytic approximations to the radial wave function

In order to evaluate the integrals which occur in section 17 it is

necessary to have analytic approximations to the radial wave function $P(r)/r$. Unless otherwise stated all the expressions given below are accurate to within 1% over the relevant range. An accurate expression for P over the whole range is

$$P_1 = r^2[0.0583 \exp(-0.54r) + 0.489 \exp(-1.144r) + 7.49 \exp(-2.71r)] + 80.6r^3 \exp(-7.27r) \quad (5.11)$$

The last term is significant over such a small region that it always makes a negligible contribution to the integrals calculated. 1% accuracy is preserved over the range $r > 3.5$ if only the first two terms of (11) are retained. An alternative fit, valid over the range $2.4 < r < 7.2$, is

$$P_2 = r^2[0.123 \exp(-0.65r) + 2.22 \exp(-1.77r)] \quad (5.12)$$

and this was used in an independent check of the nearest neighbour two-centre energy integrals.

For certain purposes it is convenient to have expressions involving terms $r^3 e^{-\alpha r}$ and such an expression, valid for $3.5 < r < 10$, is

$$P_3 = r^3[0.0233 \exp(-0.68r) + 0.502 \exp(-1.47r)] \quad . \quad (5.13)$$

In some cases much cruder single term fits were used. Thus for $r > 3.5$

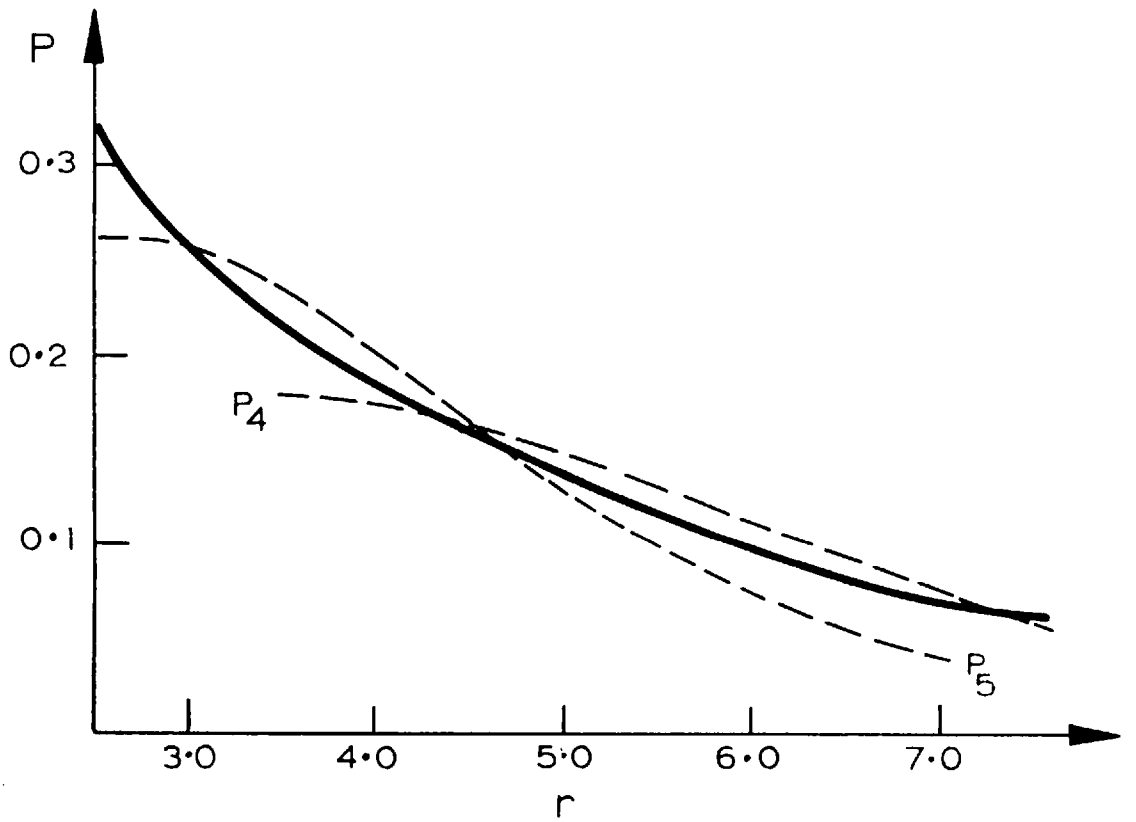

FIGURE 9: One-term approximations (broken curves) to the radial function P. (full curve)

a rough fit is given by

$$P_4 = 0.076r^3 \exp(-0.83r) \tag{5.14}$$

and for $2.4 < r < 7.2$

$$P_5 = 0.26r^3 \exp(-1.1r) , \tag{5.15}$$

P_4 and P_5 are compared with the exact curve in figure 9 and it will be seen that the fit is rather poor. The parts of the calculation employing these expressions could be improved by using two term fits but in view of the unpromising results obtained this does not appear worthwhile. An improvement in accuracy here could hardly produce the radical changes necessary to make significant improvements in the final results.

15. Expressions for the Matrix Elements

In the preceding sections all the ingredients of a tight-binding calculation were presented. The crystal potential, 'atomic' potential and 'atomic' wave functions were all specified and it remains to insert them in the formulae of section 6.2 to obtain the matrix elements in the secular equation. It is the aim of this calculation to calculate the matrix elements fairly accurately without any of the arbitrary simplifications normally made in a tight-binding calculation. To

avoid having to solve fifth-order secular equations the detailed calculation of the energy bands will be restricted to the (0,0,1) axis in $\underline{k}$-space. In this direction only the diagonal matrix elements H_{nn}, Δ_{nn} are non-zero and the secular equation factorizes completely. Thus for the (0,0,1) direction in $\underline{k}$-space the five energy bands are given by

$$E_n(\underline{k}) = H_{nn}/\Delta_{nn} = E_0 + \frac{\sum_t J_t^{(nn)} e^{-i\underline{k}\cdot\underline{R}_t}}{\sum_t S_t^{(nn)} e^{-i\underline{k}\cdot\underline{R}_t}} \qquad (n=1,..5) \tag{5.16}$$

The group-theoretical reason for the factorization of the secular equation is that for $\underline{k}$ along the (0,0,1) axis Δ, the Bloch functions f_n formed from the 'atomic' function ϕ_n, defined by (6), form bases for the irreducible representations of the group of Δ as follows:

Δ_1	Δ_2	Δ_2'	Δ_1'	Δ_5
f_5	f_4	f_1	-	(f_2, f_3)

Thus f_5, f_4 and f_1 belong to different non-degenerate representations and f_2 and f_3 belong to the doubly degenerate representation Δ_5. There are, therefore, four distinct bands to calculate along the (0,0,1) axis, one of them being doubly degenerate.

The second term on the right-hand side of (5.16) involves sums over lattice sites $\underline{R}_t$, and it is convenient now to classify these as

nearest neighbours, next nearest neighbours etc. to the lattice site at the origin. In the next section the sites are listed up to 9th nearest neighbours.

15.1 The lattice sums

The Cu lattice is face-centred cubic with lattice constant, i.e. side of the unit cube of the lattice, a = 6.03 A.U.

Nearest neighbours (12)

$a(\pm \frac{1}{2}, \pm \frac{1}{2}, 0)$, $a(\pm \frac{1}{2}, 0, \pm \frac{1}{2})$, $a(0, \pm \frac{1}{2}, \pm \frac{1}{2})$

Next nearest neighbours (6)

$a(\pm 1, 0, 0)$, $a(0, \pm 1, 0)$, $a(0, 0, \pm 1)$

3rd nearest neighbours (24)

$a(\pm 1, \pm \frac{1}{2}, \pm \frac{1}{2})$, $a(\pm \frac{1}{2}, \pm 1, \pm \frac{1}{2})$, $a(\pm \frac{1}{2}, \pm \frac{1}{2}, \pm 1)$

4th nearest neighbours (12)

$a(\pm 1, \pm 1, 0)$, $a(\pm 1, 0, \pm 1)$, $a(0, \pm 1, \pm 1)$

5th nearest neighbours (24)

$a(\pm \frac{3}{2}, \pm \frac{1}{2}, 0)$, $a(\pm \quad , 0, \pm \frac{1}{2})$, $a(\pm \frac{1}{2}, \pm \frac{3}{2}, 0)$

$a(0, \pm \frac{3}{2}, \pm \frac{1}{2})$, $a(\pm \frac{1}{2}, 0, \pm \frac{3}{2})$, $a(0, \pm \frac{1}{2}, \pm \frac{3}{2})$

6th nearest neighbours (8)

$a(\pm 1, \pm 1, \pm 1)$

7th nearest neighbours (48)

$a(\pm \frac{3}{2}, \pm 1, \pm \frac{1}{2})$, $a(\pm \frac{3}{2}, \pm \frac{1}{2}, \pm 1)$, $a(\pm 1, \pm \frac{3}{2}, \pm \frac{1}{2})$

$a(\pm \frac{1}{2}, \pm \frac{3}{2}, \pm 1)$, $a(\pm 1, \pm \frac{1}{2}, \pm \frac{3}{2})$, $a(\pm \frac{1}{2}, \pm 1, \pm \frac{3}{2})$

8th nearest neighbours (6)

$$a(\pm 2,\ 0,\ 0) \quad , \quad (a(0,\ \pm 2,\ 0) \quad , \quad a(0,\ 0,\ \pm 2)$$

9th nearest neighbours (36)

$$a(\pm\tfrac{3}{2},\ \pm\tfrac{3}{2},\ 0) \quad , \quad a(\pm\tfrac{3}{2},\ 0,\ \pm\tfrac{3}{2}) \quad , \quad a(0,\ \pm\tfrac{3}{2},\ \pm\tfrac{3}{2})$$

$$a(\pm 2,\ \pm\tfrac{1}{2},\ \pm\tfrac{1}{2}) \quad , \quad a(\pm\tfrac{1}{2},\ \pm 2,\ \pm\tfrac{1}{2}) \quad , \quad a(\pm\tfrac{1}{2},\ \pm\tfrac{1}{2},\ \pm 2)$$

The sum in the numerator of 5.16 will presently be written out in full up to 8th nearest neighbours. It may first be noted that, omitting the complex conjugate symbol in (2.20) since the 'atomic' functions used here are real,

$$\begin{aligned} J_{\underline{R}}^{(nn)} &= \int \phi_n(\underline{r} - \underline{R})[V - U]\phi_n(\underline{r})\,d\tau \\ &= \int \phi_n(\underline{r} + \underline{R})[V - U]\phi_n(\underline{r})\,d\tau \\ &= J_{-\underline{R}}^{(nn)} \end{aligned}$$

This follows from the fact that V, U, and all the ϕ_n are invariant under inversion in the origin ($\underline{r} \rightarrow -\underline{r}$).

Thus

$$\sum_t J_t^{(nn)} \exp(-i\underline{k}\cdot\underline{R}_t) = J_o^{(nn)} + \sum_{t \neq o} J_t^{(nn)} \cos \underline{k}\cdot\underline{R}_t \qquad (5.17)$$

It is convenient to use the obvious notation $J_{(pqr)}^{(nn)}$ to denote $J_t^{(nn)}$ with $\underline{R}_t = a(p,\ q,\ r)$ and the following expressions for the

sum (5.17) with $\underline{k} = (0, 0, 2\gamma/a)$ are easily obtained. The sum is given in two parts, the first part up to 4th nearest neighbours and the second part from 5th to 9th nearest neighbours. This is done because the contributions of neighbours up to fourth have been calculated more carefully than the higher order contributions and it is desirable to examine how important the higher order contributions are. The superscripts (nn) are omitted in the formulae below

$$\sum J_t \exp(-i\underline{k}\cdot\underline{R}_t)$$

(1st - 4th n.n.)

$$= J_0 + 4J(\tfrac{1}{2}\,\tfrac{1}{2}\,0) + 2J(1\,0\,0) + 2J(0\,1\,0) + 4J(1\,1\,0$$
$$+\left[4J(0\,\tfrac{1}{2}\,\tfrac{1}{2}) + 4J(\tfrac{1}{2}\,0\,\tfrac{1}{2}) + 8J(1\,\tfrac{1}{2}\,\tfrac{1}{2}) + 8J(\tfrac{1}{2}\,1\,\tfrac{1}{2})\right]\cos\gamma$$
$$+\left[2J(0\,0\,1) + 8J(\tfrac{1}{2}\,\tfrac{1}{2}\,1) + 4J(0\,1\,1) + 4J(1\,0\,1)\right]\cos 2\gamma$$

(5.18)

$$\sum_{(s^n_{n.n.}-q^n)} J_t \exp(-i\underline{k}\cdot\underline{R}_t)$$

$$= 4J_{(\frac{1}{2}\frac{3}{2}0)} + 4J_{(\frac{3}{2}\frac{1}{2}0)} + 2J_{(2\,0\,0)} + 2J_{(0\,2\,0)} + 4J_{(\frac{3}{2}\frac{3}{2}0)}$$

$$+ \left[4J_{(\frac{3}{2}0\frac{1}{2})} + 4J_{(0\frac{3}{2}\frac{1}{2})} + 8J_{(\frac{3}{2}\,1\,\frac{1}{2})} + 8J_{(1\frac{3}{2}\frac{1}{2})} + 8J_{(2\,\frac{1}{2}\,\frac{1}{2})} + 8J_{(\frac{1}{2}\,2\,\frac{1}{2})}\right]\cos\gamma$$

$$+ \left[8J_{(1\,1\,1)} + 8J_{(\frac{3}{2}\,\frac{1}{2}\,1)} + 8J_{(\frac{1}{2}\frac{3}{2}\,1)}\right] \cos 2\gamma$$

$$+ \left[4J_{(\frac{1}{2}\,0\,\frac{3}{2})} + 4J_{(0\,\frac{1}{2}\,\frac{3}{2})} + 8J_{(\frac{1}{2}\,1\,\frac{3}{2})} + 8J_{(1\,\frac{1}{2}\,\frac{3}{2})} + 4J_{(0\frac{3}{2}\frac{3}{2})} + 4J_{(\frac{3}{2}\,0\,\frac{3}{2})}\right] \cos 3\gamma$$

$$+ \left[8J_{(\frac{1}{2}\,\frac{1}{2}\,2)} + 2J_{(0\,0\,2)}\right] \cos 4\gamma \quad . \tag{5.19}$$

It is unnecessary to calculate $J^{(nn)}_{(pqr)}$ for both n = 1 and 2 since it follows from cyclic permutation of the integration variables that

$$J^{(11)}_{(pqr)} = J^{(22)}_{(rpq)} \tag{5.20}$$

The next four sections are devoted to the method of calculating $J^{(nn)}_{(pqr)}$ appearing in (5.18) and (5.19) with n = 1, 4 and 5. Formulae exactly similar to (5.18) and (5.19) exist for the sum in the denominator of (5.16) and the calculation of the $S^{(nn)}_{(pqr)}$ is also discussed

below.

16. Reduction of the non-orthogonality and energy integrals

For symmetry reasons all the integrals $J^{(nn)}_{(pqr)}$ and $S^{(nn)}_{(pqr)}$ are not independent, i.e. linear relations exist between them, and the aim of this section is to reduce their calculation to calculating a smaller number of independent integrals. Slater and Koster (1954) have discussed this problem to some extent and have given a general prescription for dealing with two-centre integrals. They point out that Fletcher (1952) in his calculation for Ni calculated twice as many integrals as was necessary and this sort of unnecessary labour must be avoided in a calculation as complex as the present one. Slater and Koster also discussed in special cases the problems of reducing $J^{(nn)}_{(pqr)}$ when the two centre approximation is not made. However they gave no general prescription for doing this and the sets of independent integrals they used are not the most convenient ones for calculation. This last consideration, which is discussed again in section 16.3, was not important to Slater and Koster as their independent integrals were treated as disposable parameters.

16.1 Notation for the integrals

Before proceeding with the reduction of the non-orthogonality and energy integrals it is convenient to introduce a slightly modified notation. Different notations are better for different purposes and so far two notations have been used to specify integrals. In the

general theory of section 6.2 a single suffix t was used to denote a particular lattice site $\underline{R}_t$ and the corresponding non-orthogonality and energy integrals were denoted by $S_t^{(nn)}$ and $J_t^{(nn)}$ respectively. In the explicit formulae (5.18) and (5.19) it was necessary to specify the co-ordinates of each lattice site so that $J_t^{(nn)}$ was replaced by $J_{(pqr)}^{(nn)}$ where $\underline{R}_t = a(p, q, r)$. A similar notation $S_{(p,q,r)}^{(nn)}$ was implied for non-orthogonality integrals. In the following it will be useful to specify a lattice site as $\underline{R}_{tu}$ where the first suffix indicates that it is a t^{th} nearest neighbour (to the origin) and the second suffix u indicates the particular neighbour. The corresponding non-orthogonality and energy integrals will be denoted by $S_{tu}^{(nn)}$ and $J_{tu}^{(nn)}$.

16.2 Non-orthogonality integrals

The integrals

$$S_{tu}^{(nn)} = \int \phi_n(\underline{r} - \underline{R}_{tu})\, \phi_n(\underline{r})\, d\tau \qquad (5.21)$$

are easily reduced by expressing the original d functions (5.6), which are referred to the cubic axes of the crystal, in terms of d functions referred to axes Ox', Oy', Oz' where Oz' is in the direction of $\underline{R}_{tu}$. Suppose Ox', Oy' Oz' have direction cosines (l_1, m_1, n_1), (l_2, m_2, n_2) and (l, m, n) respectively, referred to the cubic axes Oxyz. Then, if $\phi_{1'}(\underline{r})$ denotes $[15/(4\pi)]^{\frac{1}{2}}$ $(x'y'/r^2)$ f(r) and $\phi_{2'}(\underline{r})$ denotes $[15/(4\pi)]^{\frac{1}{2}}$ $(y'z'/r^2)$ f(r) etc., the following relations are easily

obtained

$$\phi_1 = (l_1 m_2 + l_2 m_1)\phi_{1'} + (l_2 m + l m_2)\phi_{2'} + (l m_1 + l_1 m)\phi_{3'}$$
$$+ (2 l_1 m_1 + l m)\phi_{4'} + \sqrt{3}\, l m \phi_{5'}$$

$$\phi_4 = (l_1 l_2 - m_1 m_2)\phi_{1'} + (l_2 l - m_2 m)\phi_{2'} + (l l_1 - m m_1)\phi_{3'}$$
$$+ \left[l_1^2 - m_1^2 + \tfrac{1}{2}(l^2 - m^2)\right]\phi_{4'} + (\sqrt{3}/2)(l^2 - m^2)\phi_{5'}$$

$$\phi_5 = \sqrt{3}\, n_1 n_2 \phi_{1'} + \sqrt{3}\, n_2 n \phi_{2'} + \sqrt{3}\, m n_1 \phi_{3'} + (\sqrt{3}/2)(n_1^2 - n_2^2)\phi_{4'}$$
$$+ \tfrac{1}{2}(3n^2 - 1)\phi_{5'} \quad . \qquad (5.22)$$

It may easily be shown that the integral

$$S_t^{(n'm')} = \int \phi_{n'}(\underline{r} - \underline{R}_{tu})\, \phi_{m'}(\underline{r})\, d\tau \qquad (5.23)$$

is zero unless $n' = m'$ and that

$$S_t^{(1'1')} = S_t^{(4'4')} \; ; \quad S_t^{(2'2')} = S_t^{(3'3')} \; . \qquad (5.24)$$

It is clear that $S_t^{(n'm')}$ does not depend on the particular neighbour $\underline{R}_{tu}$ so the second suffix u need not be appended. The integrals (5.21) may be expressed in terms of the integrals (5.23) by substituting for

the ϕ_n from (5.22) and using the relations between direction cosines of orthogonal axes. One obtains

$$S_{tu}^{(11)} = (n^2 + l^2m^2)S_t^{(1'1')} + (l^2 + m^2 - 4l^2m^2)S_t^{(2'2')} + 3l^2m^2S_t^{(5'5')}$$

$$S_{tu}^{(44)} = [n^2 + \tfrac{1}{4}(l^2 - m^2)]S_t^{(1'1')} + [l^2 + m^2 - (l^2 - m^2)^2]S_t^{(2'2')} + \tfrac{3}{4}(l^2 - m^2)^2 S_t^{(6'6')} \qquad (5.25)$$

$$S_{tu}^{(55)} = \tfrac{3}{4}(l^2 + m^2)\, S_t^{(1'1')} + 3n(l^2 + m^2)S_t^{(2'2')} + [n^2 - \tfrac{1}{4}(l^2 + m^2)^2]S_t^{(5'5')}$$

Thus three integrals must be calculated for each value of $|\underline{R}_t|$. Exactly similar relations hold for two-centre energy integrals in which an additional factor U(r) occurs in the integrands of (5.21) and (5.23). These relations have been given previously by Slater and Koster (1954). The coefficients of $S_t^{(n'n')}$ in (5.25) are listed in table 2 for all neighbours up to fourth nearest neighbours. The co-efficients for more distant neighbours are easily calculated from (5.25)

16.3. Energy Integrals

To reduce the integrals

$$J_{tu}^{(nn)} = \int \phi_n(\underline{r} - \underline{R}_{tu})[V(\underline{r}) - U(r)]\phi_n(\underline{r})d\tau \qquad (5.26)$$

to a sum of independent integrals it is once again convenient to express the integrand in terms of d functions referred to axes $Ox'y'z'$, such that Ox' is in the direction of $\underline{R}_{tu}$. The integrals (5.26) are then obtained in terms of integrals defined by

$$J_t^{(n'm')} = \int \phi_{n'}(\underline{r} - \underline{R}_{tu})[V(\underline{r}) - U(r)]\phi_{m'}(\underline{r})d\tau \; . \qquad (5.27)$$

The specification of the Ox' and Oy' axes, which is necessary to complete this definition, is discussed later for each group of neighbours. The axes are to be chosen in an equivalent way for each neighbour of a group, so that $J_t^{(n'm')}$ depends only on the type of neighbour and the second suffix u can be dropped.

Slater and Koster did not use the integrals (5.27); they selected a certain number of independent $J_t^{(nm)}$ and expressed all other integrals $J_t^{(nm)}$ in terms of these. For example all the nearest neighbour integrals of the face-centred cubic lattice

were expressed in terms of the six integrals

$$J^{(11)}_{(\frac{1}{2}\frac{1}{2}0)} \qquad J^{(11)}_{(0\frac{1}{2}\frac{1}{2})} \qquad J^{(13)}_{(0\frac{1}{2}\frac{1}{2})}$$

$$J^{(15)}_{(\frac{1}{2}\frac{1}{2}0)} \qquad J^{(55)}_{(\frac{1}{2}\frac{1}{2}0)} \qquad J^{(44)}_{(\frac{1}{2}\frac{1}{2}0)} \quad .$$

It is clear that Slater and Koster were obliged to consider off-diagonal integrals $J_t^{(nm)}$, $n \neq m$. The procedure used here also involves integrals $J_t^{(n'm')}$ with $n' \neq m'$. The disadvantage of Slater and Koster's method of reduction is only apparent when one actually attempts to calculate their independent integrals. It is then not easy to see how many independent three-centre integrals must be calculated. When integrals $J_t^{(n'm')}$ are used involving d functions referred to specially chosen axes $Ox'y'z'$, it is possible to consider the three-centre integrals in groups of 2, 4 or even 8 equal ones. The details of this procedure are given in section 17.3.

In the case of non-orthogonality integrals and two-centre energy integrals the choice of the direction of Ox' is arbitrary and the direction cosines of Ox' and Oy' do not appear in the formulae (5.25). However in the case of $J_{tu}^{(nm)}$, since $V(\underline{r})$ does not have complete rotational symmetry about the line R_{tu}, it is

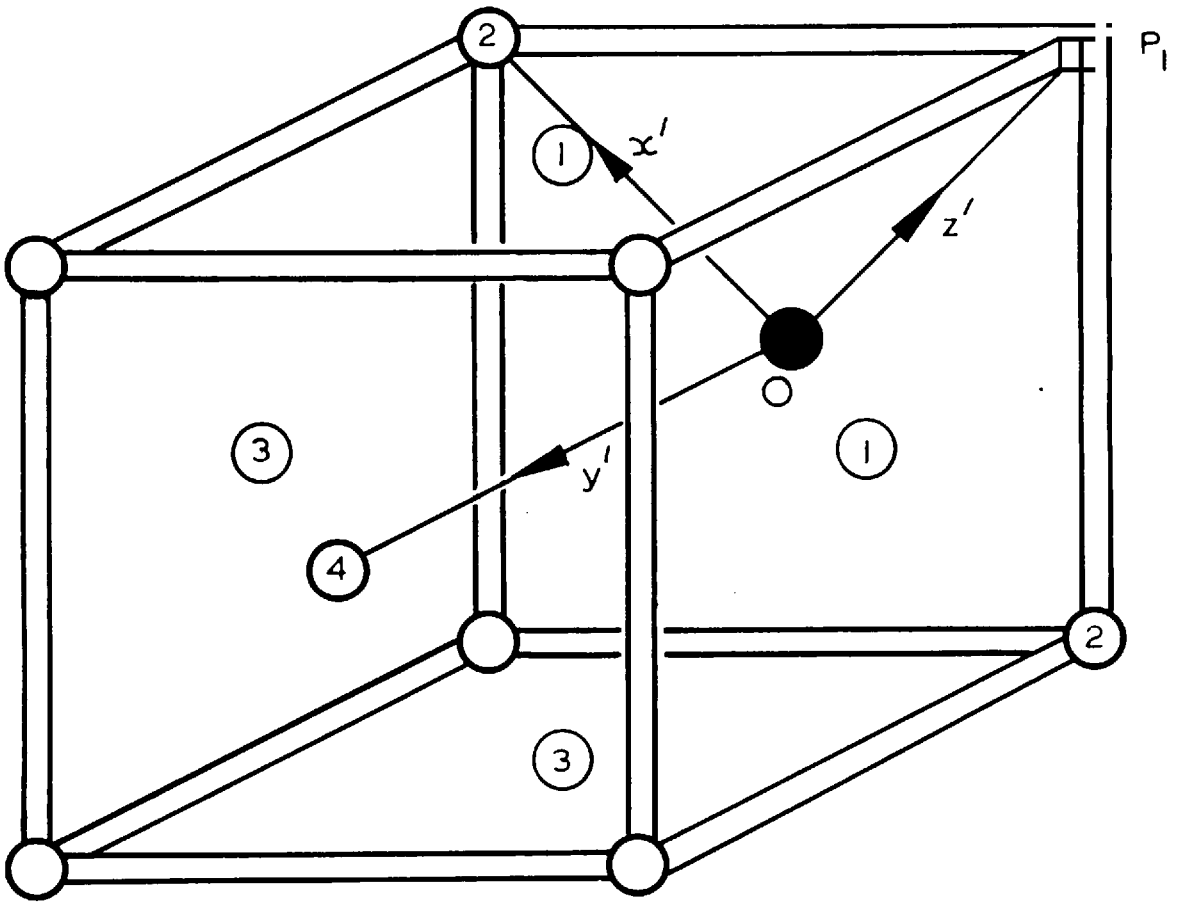

FIGURE Transformed axes $Ox'y'z'$ for nearest neighbour energy integrals. Numbered sites refer to Table II; other centres included there are obtained by reflecting the numbered ones in the $x'z'$ plane and in the plane which perpendicularly bisects OP_1.

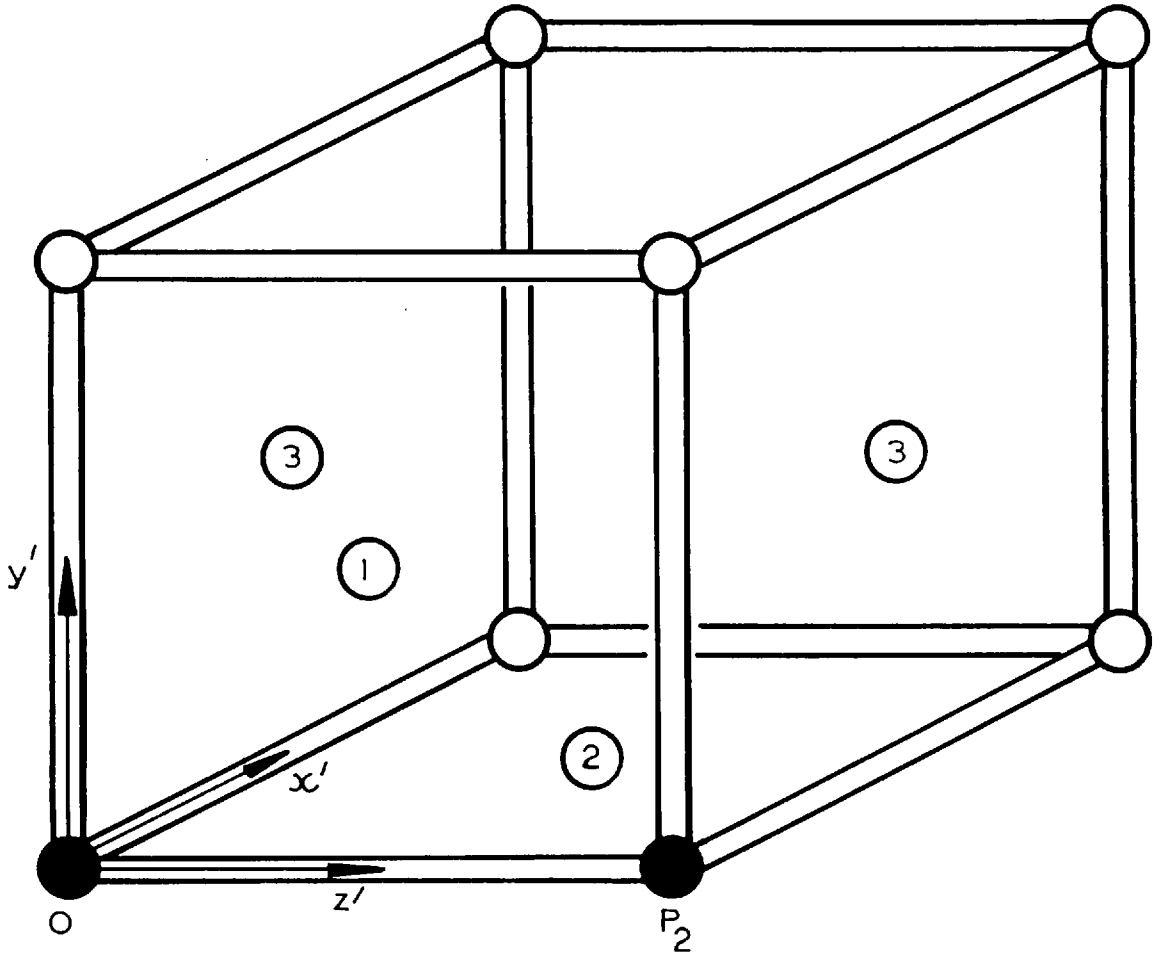

FIGURE Transformed axes $Ox'y'z'$ for next nearest neighbour energy integrals. Numbered sites refer to Table 12; other centres included there are obtained by reflecting the numbered ones in the planes $x'=0$ and $y'=0$.

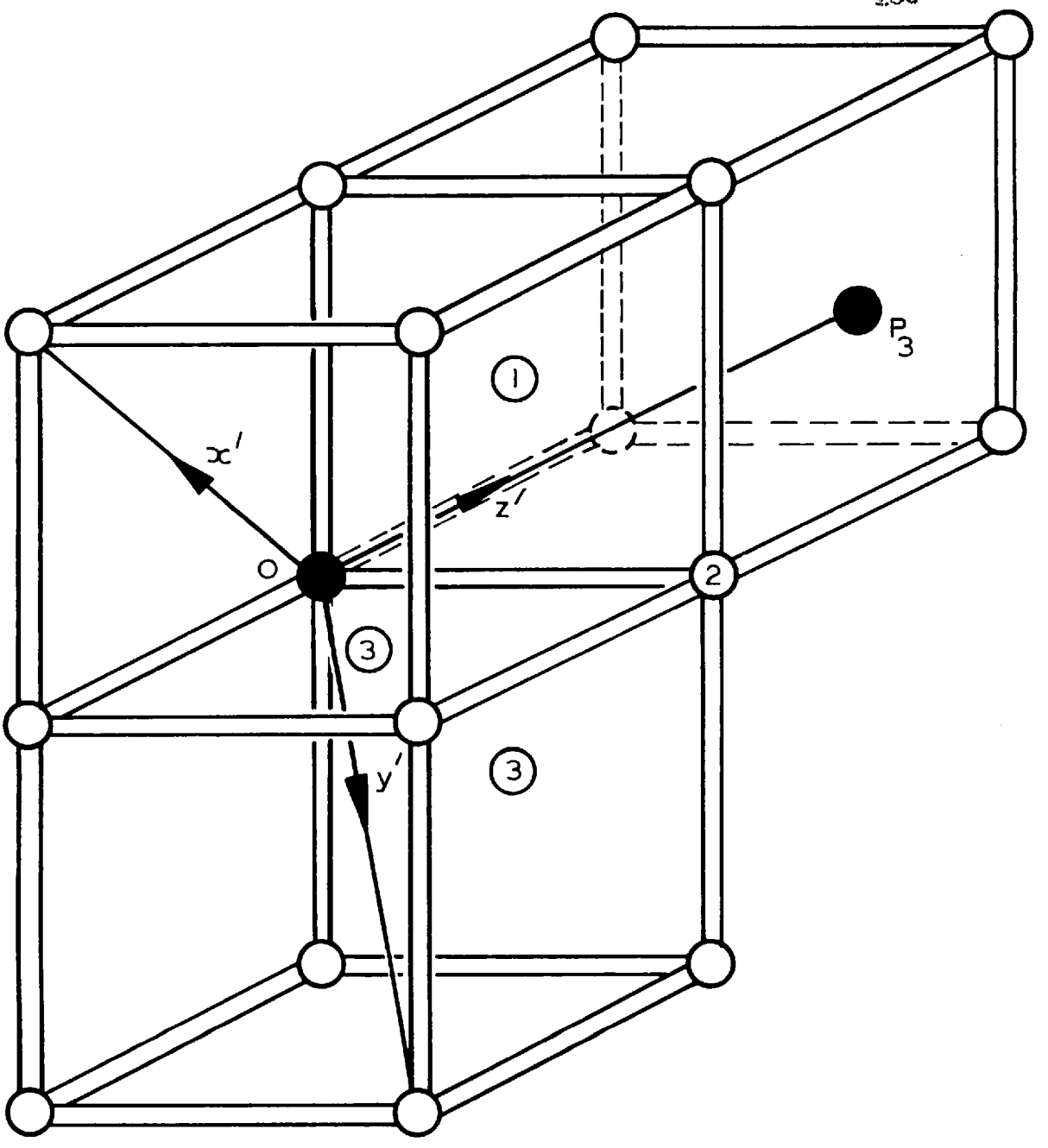

FIGURE Transformed axes $Ox'y'z'$ for 3rd nearest neighbour energy integrals. Numbered centres refer to Table 13; other centres included there are obtained by reflecting the numbered ones in the mid-point of OP_3

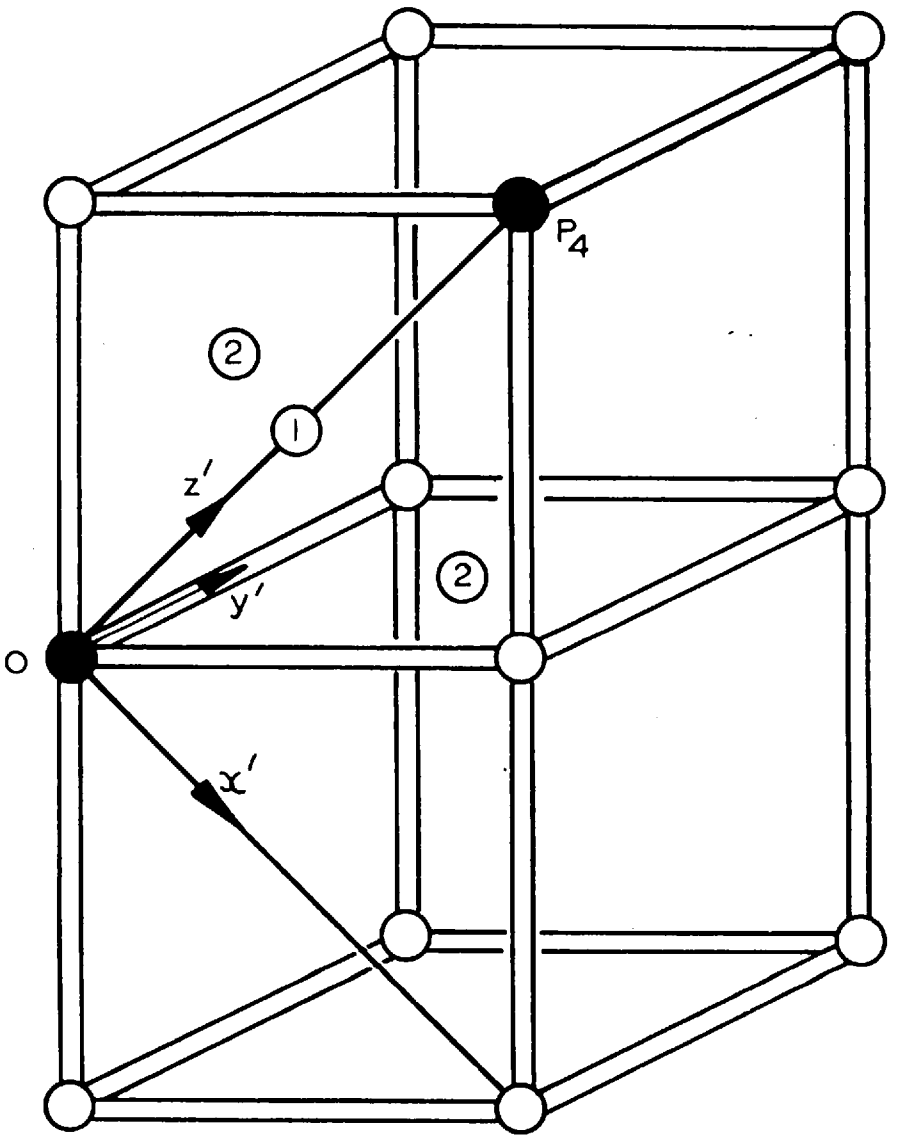

FIGURE Transformed axes O x′y′z′ for 4th nearest neighbour energy integrals. Numbered centres refer to Table 14; other centres included there are obtained by reflecting the numbered ones in the x′z′ plane and the plane which perpendicularly bisects O P_4.

necessary to choose the x' and y' axes in the most convenient way for each lattice site $\underline{R}_{tu}$.

Nearest Neighbours

Consider first the case where $\underline{R}_{tu}$ is a nearest neighbour. It is convenient to take Oy' along a cubic axis and the axes Ox'y'z' are shown in figure 10 for the case $\underline{R}_{tu} = a(\frac{1}{2}, 0, \frac{1}{2})$. it is not difficult to find which of the integrals $J_1^{(n's')}$ are non-zero. This is done by inspecting the irreducible representations of the group of the nearest neighbour axis i.e. the group of operations under which the lattice and any point of the nearest neighbour axis remain invariant. The character table for this group is given in table 5 [c.f. Jones (1960) p.107] and the type of d function $\phi_{n'}$ belonging to each representation is indicated in the last column. The operations in each class are given in the usual notation but referred to the Ox'y'z' system of axes (e.g. $\bar{x}'y'z'$ denotes the operations $x' \rightarrow -x'$, $y' \rightarrow y'$, $z' \rightarrow z'$, or reflection in the y'z' plane). The integral (5.27) is non-zero only when $\phi_{n'}$ and $\phi_{m'}$ belong to the same irreducible representation and so the integrals to be calculated are

$$J_1^{(1'1')}, \quad J_1^{(2'2')}, \quad J_1^{(3'3')}, \quad J_1^{(4'4')}, \quad J_1^{(5'5')}, \quad J_1^{(4'5')} = J_1^{(5'4')}.$$

The last two integrals are equal since the contribution of the U

term in V - U is zero when $n' \neq m'$ and V has reflection symmetry about the plane which perpendicularly bisects the line OP_1 in figure 10; also ϕ_4, and ϕ_5, are invariant under the substitution $z' \rightarrow -z'$. By using equation (5.22), and the notation used there for the direction cosines of Ox', Oy' Oz', one obtains the following expressions for the nearest neighbour integrals $J_{1u}^{(nn)}$ in terms of $J_1^{(n'm')}$:

$$J_{1u}^{(11)} = (l_1m_2 + l_2m_1)^2 J_1^{(1'1')} + (l_2n + lm_2)^2 J_1^{(2'2')}$$
$$+ (lm_1 + l_1m)^2 J_1^{(3'3')} + (2l_1m_1 + ln)^2 J_1^{(4'4')}$$
$$+ 3l^2m^2 J_1^{(5'5')} + 2\sqrt{3}\, lm(2l_1m_1 + ln) J_1^{(4'5')}$$

$$J_{1u}^{(44)} = (l_1l_2 - m_1m_2)^2 J_1^{(1'1')} + (l_2l - m_2n)^2 J_1^{(2'3')}$$
$$+ (ll_1 - nm_1)^2 J_1^{(3'3')} + [l_1^2 - m_1^2 + \tfrac{1}{2}(l^2 - m^2)]^2 J_1^{(4'4')}$$
$$+ \tfrac{3}{4}(l^2 - m^2)^2 J_1^{(5'5')} + \sqrt{3}(l^2 - m^2)\,[l_1^2 - m_1^2 + \tfrac{1}{2}(l^2 - m^2)] J_1^{(4'5')}$$

$$J_{1u}^{(55)} = 3n_1^2 n_2^2 J_1^{(1'1')} + 3n_2^2 n_3^2 J_1^{(2'2')} + 3n_1^2 n_3^2 J_1^{(3'3')}$$

$$+ \tfrac{3}{4}(n_1^2 - n_3^2)^2 J_1^{(4'4')} + \tfrac{1}{4}(3n^2 - 1)^2 J_1^{(5'5')}$$

$$+ \tfrac{\sqrt{3}}{2}(3n^2 - 1)(n_1^2 - n_3^2) J_1^{(4'5')} \qquad (5.28)$$

Particular cases are obtained from (5.28) by substituting the relevant value of the direction cosines. For example in the case $R_{1u} = a(\frac{1}{2}, 0, \frac{1}{2})$ one substitutes

$$(l\ m\ n) = (\sqrt{\tfrac{1}{2}}\ 0\ \sqrt{\tfrac{1}{2}}) \cdot (l_1\ m_1\ n_1) = (-\sqrt{\tfrac{1}{2}}\ 0\ +\sqrt{\tfrac{1}{2}})$$

$$(l_2\ m_2\ n_2) = (0\ -1\ 0)$$

The coefficients of the $J_1^{(n'n')}$ in these formulae are listed in table 6 for $R_{1u} = a(\frac{1}{2},0,\frac{1}{2})$, $a(0,\frac{1}{2},\frac{1}{2})$ and $a(\frac{1}{2},\frac{1}{2},0)$

Next nearest neighbours

$0x'$, $0y'$, $0z'$ may be chosen to be cubic axes as shown in figure II. The character table for the group of a cubic axis is given in table 4 and it follows that the only non-zero integrals (5.27) are

$$J_2^{(1'1')}, \quad J_2^{(2'2')} = J_2^{(3'3')}, \quad J_2^{(4'4')}, \quad J_2^{(5'5')}.$$

Equations exactly analogous to (5.28) may be written down expressing $J_{2u}^{(nn)}$ in terms of the above integrals and the coefficient of these

are listed in table 7.

Third nearest neighbours

It is convenient to take Ox' in a nearest neighbour direction and Oy' in a sixth nearest neighbour direction as shown in figure 12 for the case $\underline{R}_{3u} = a(1, \frac{1}{2}, \frac{1}{2})$. The direction cosines of the axes Ox'y'z', referred to Oxyz, for this case are

$$Ox' \qquad (0, -\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}})$$

$$Oy' \qquad (\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}}, -\frac{1}{\sqrt{3}})$$

$$Oz' \qquad (\sqrt{\frac{2}{3}}, \frac{1}{\sqrt{6}}, \frac{1}{\sqrt{6}}) \quad .$$

The symmetry about the Oz' axis is very low in this case and the group of the axis consists only of the identity operator and reflection in the y'z' plane. The trivial character table is given in table 5 and it follows that the non-zero integrals (5.27) are

$$J_3^{(1'1')} \quad J_3^{(2'2')} \quad J_3^{(3'3')} \quad J_3^{(4'4')} \quad J_3^{(5'5')} \qquad (5.29)$$

$$J_3^{(4'5')} = J_3^{(5'4')}, \quad J_3^{(2'5')} = J_3^{(5'2')}$$

$$J_3^{(2'4')} = J_3^{(4'2')}, \quad J_3^{(1'3')} = J_3^{(3'1')} \quad .$$

The last four pairs of integrals are equal since U can be omitted in the integrand and $V(\underline{r})$ is invariant under reflection in the mid-point of the line OR_s in figure 12. The effect of this reflection operation is $\underline{r} \rightarrow \underline{R}_{su} - \underline{r}$ and hence, from (5.37), one finds $J_s^{(n'm')} = J_s^{(m'n')}$ by using the fact that $\phi_m(\underline{r}) = \phi_m(-\underline{r})$. The coefficients of the integrals (5.37) in expressions for $J_{su}^{(nn)}$ are given in table 8.

Fourth nearest neighbours

These are in the same directions as the nearest neighbours but twice as distant. The axes $Ox'y'z'$ may therefore be chosen as for nearest neighbours and table 6 applies.

A partial check on the tables is that tables 6, 7 and 8 must reduce essentially to table 2 if a two-centre approximation is made. In this approximation $J_t^{(n'm')} = 0$ for $n' \neq m'$ and

$$J_t^{(1'1')} = J_t^{(4'4')} \quad , \quad J_t^{(2'2')} = J_t^{(3'3')}$$

Thus the sum of the coefficients of $J_t^{(1'1')}$ and $J_t^{(4'4')}$ given by tables 6, 7 and 8 must equal the corresponding coefficients of $S_t^{(1'1')}$ in table 2. Similarly the sum of the coefficients of $J_t^{(2'2')}$ $J_t^{(3'3')}$ must equal the coefficient of $S_t^{(2'2')}$. Also the coefficients of $J_t^{(5'5')}$ must equal the corresponding coefficients of $S_t^{(5'5')}$. The equalities may readily be verified from the tables.

Neighbours more distant than the fourth will not be discussed

here since, as explained later, a two-centre approximation was used for these. No discussion has been given of $J_0^{(nn)}$ and this very special case is dealt with at the numerical stage in section 17.2.

17. Calculation of the Integrals

The next problem is actually to calculate the integrals $S_t^{(n'n')}$ and $J_t^{(n'm')}$. The decomposition of $J_t^{(n'm')}$ into two-centre and three-centre integrals is effected by substituting (2.1) for $V(\underline{r})$ in (5.27). Thus for $t \neq 0$ it is possible to write

$$J_t^{(n'm')} = F_t^{(n'm')} + G_t^{(n'm')} \tag{5.30}$$

where the first term is the two-centre contribution and the second the three-centre contribution. If it is remembered that $U(r)=v(r)$ for $r < r_o$ the two centre contribution may be written

$$F_t^{(n'm')} = \left[-E_t^{(n'n')} + I_t^{(n'n')}\right] \delta_{n'm'} \tag{5.31}$$

where

$$E_t^{(n'n')} = \int_{(\bar{o})} \phi_{n'}(\underline{r} - \underline{R}_t)\, U(r) \phi_{n'}(\underline{r}) d\tau , \tag{5.32}$$

$$I_t^{(n'n')} = \int_{(o)} \phi_{n'}(\underline{r} - \underline{R}_t)\, U(r) \phi_{n'}(r) d\tau , \tag{5.33}$$

and $\int_{(o)}$, $\int_{(\bar{o})}$ denote integrations over the regions inside and outside the sphere radius r_o surrounding the origin. The three-centre

contribution is given by

$$G_t^{(n'm')} = \sum_{i \neq o,t} T_{ti}^{(n'm')} \qquad (5.34)$$

where

$$T_{ti}^{(n'm')} = \int_{(i)} \phi_{n'}(\underline{r} - \underline{R}_t)\, U(\underline{r} - \underline{R}_i)\phi_{m'}(\underline{r})\, d\tau \qquad (5.35)$$

and $\int_{(i)}$ denotes integration within the sphere surrounding $\underline{R}_i$.

17.1 Two-centre integrals

Probably the most generally useful method of calculating two-centre integrals is that of Barnett and Coulson (1951) and this is the method adopted here for calculating the $I_t^{(n'n')}$ and some of the $E_t^{(n'n')}$. The method consists in expanding the radial wave function associated with one centre in a Legendre polynomial series about the other centre.

Consider first

$$I_t^{(n'n')} = \frac{15}{4\pi} \int_{(o)} \frac{x'y'}{r_t^2} f(r_t)\, U(r)\, \frac{x'y'}{r^2} f(r)\, d\tau \qquad (5.36)$$

where $r_t = |\underline{r} - \underline{R}_t|$. If $f(r_t)$ is written in the form

$$f(r_t) = r_t \sum_i A_i e^{-\alpha_i r_t} \qquad (5.37)$$

then

$$I_t^{(i'i')} = \frac{15}{4\pi} \sum_i A_i \int_{(o)} \frac{e^{-\alpha_i r_t}}{r_t} U(r)\rho(r) \frac{x'^2 y'^2}{r^3} d\tau \quad (5.38)$$

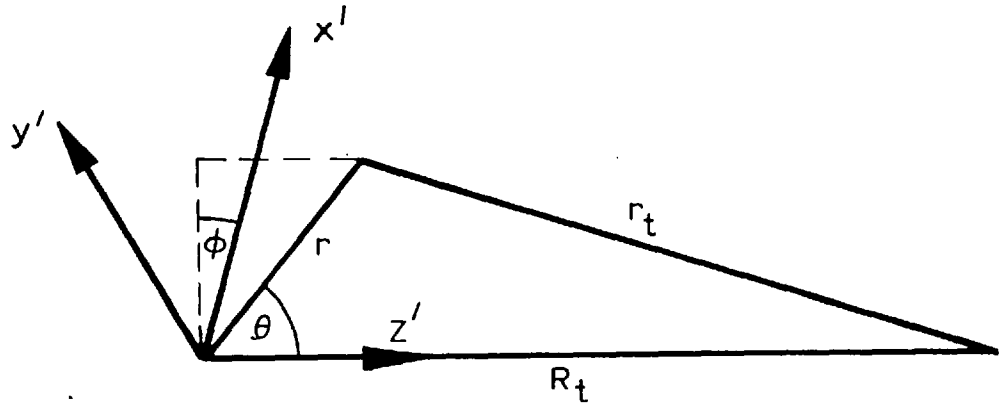

Fig. 14

The whole integrand in (5.38) may be expressed in polar co-ordinates r, θ, φ (see figure 14) by using the expansion

$$\frac{e^{-\alpha r_t}}{r_t} = \sum_{n=0}^{\infty} \frac{2n+1}{\sqrt{r R_t}} P_n(\cos\theta) I_{n+\frac{1}{2}}(\alpha r) K_{n+\frac{1}{2}}(\alpha R_t) \quad (5.39)$$

which is valid for $r<|R_t|$ and is therefore valid over the sphere of radius r_o surrounding the origin. After substituting (5.39) in (5.38) and carrying out the φ and θ integrations one obtains

$$I_t^{(1'1')} = R_t^{-\frac{1}{2}} \sum_i A_i \left\{ K_{\frac{1}{2}}(\alpha_i R_t) H_{20}(\alpha_i) - \frac{10}{7} K_{\frac{5}{2}}(\alpha_i R_t) H_{22}(\alpha_i) + \frac{3}{7} K_{\frac{9}{2}}(\alpha_i R_t) H_{24}(\alpha_i) \right\} \tag{5.40}$$

where

$$H_{pn}(\alpha) = \int_0^{r_o} r^{p+\frac{1}{2}} U(r) P(r) J_{n+\frac{1}{2}}(\alpha r) dr. \tag{5.41}$$

In the same way, and using recurrence formulae for the modified Bessel functions, $I_t^{(2'2')}$ and $I_t^{(3'3')}$ may be expressed in terms of the same radial integrals $H_{20}(\alpha_i)$, $H_{22}(\alpha_i)$ and $H_{24}(\alpha_i)$. Once these integrals have been calculated for the appearing in (5.37), the formula (5.40) enables one to calculate $I_t^{(1'1')}$ for all neighbour distances R_t, and similarly for $I_t^{(2'2')}$ and $I_t^{(3'3')}$. The first three terms in (5.11), which give an excellent fit to P for $r > r_o$, were used to express $f(r_t)$ in the form (5.37) and the three radial integrals $H_{2n}(\alpha_i)$, $n = 0, 2, 4$ were evaluated numerically for $\alpha_i = 0.54$, 1.44 and 3.71. The numerical integration was done using Simpson's rule with 12 intervals and values of the half-order modified Bessel functions were

taken from the tables by O.M. Jones (1956). The integrals $I_t^{(n'n')}$ obtained from (5.40) and similar expressions are tabulated up to 4th nearest neighbours in table 9. The $I_t^{(n'n')}$ are negligible compared with the corresponding $E_t^{(n'n')}$ for more distant neighbours. The whole procedure was checked by using another fit to the radial wave function $f(r_t)$, viz. expression (5.12) (which is valid for nearest neighbour integrals), and the $I_1^{(n'n')}$ agreed with the values obtained previously to within 0.5%. It was unfortunately not possible to maintain this sort of accuracy throughout the calculation and still keep the work within reasonable bounds. However, the two-centre contributions to nearest and next neighbour energy integrals are believed to be accurate to within 1%. All computation was done on a desk machine.

To calculate the integrals $E_t^{(n'n')}$, defined by (5.32), it is convenient to divide the region of integration into three parts:

(a) $\quad 2.41 < r < 3.52$

(b) $\quad 3.52 < r < R_s$

(c) $\quad R_t < r < \infty$

The somewhat arbitrary division at $r = 3.52$ is made because for $r > 3.52$ simple and accurate analytic approximations are available for $U(r)$ and $P(r)$, whereas in region (a) the radial integrals are most easily calculated numerically as in $I_t^{(n'n')}$. In regions (a) and

(b) formulae such as (5.40) were used except that the limits in the radial integrals $\Pi_{pn}(\alpha)$ were changed appropriately. For region (c) formulae such as (5.40) become modified since, for $r > R_t$, r and R_t must be interchanged in the expansion (5.39). However, the formulae are basically similar. Since regions (b) and (c) surround the centre at R_t, a term corresponding to the fourth term in (5.11) should be included in (5.37) in addition to the terms with $\alpha_i = 0.54$, 1.144 and 2.71. However it may be shown that the additional term makes negligible contribution to the integrals. The radial integrals in regions (b) and (c) were calculated from analytic formulae obtained by using the exact analytic formulae for the half-order Bessel functions, expression (5.5) for U(r), and expression (5.13) and the first two terms in (5.12) for P(r) in regions (b) and (c) respectively. The accuracy of analytic methods was desirable for these radial integrals since in many cases there was considerable loss of accuracy due to cancellation between the three terms in formulae like (5.40). However, substitution in the analytic formulae for these integrals proved a long and tedious process and the method was in fact only used for first and second nearest neighbour integrals. The following quite different, somewhat cruder, method was used for integration over regions (b) and (c) together in the case of more distant neighbours.

For $r > 3.52$ a rough fit to P is given by P_4 [eqn. (5.14)]

and U may be approximated by U_2 [eqn.(5.5)]. Thus if $\phi^{(4)}_{n'}$ denotes one of the d functions with radial wave function given by r^2P_4,

$$\int_{r>3.52} \phi_{n'}(\underline{r}-\underline{R}_t)\,U(r)\,\phi_{n'}(\underline{r})\,d\tau$$

$$\simeq \int \phi^{(4)}_{n'}(\underline{r}-\underline{R}_t)\,U_2(r)\,\phi^{(4)}_{n'}(\underline{r})\,d\tau$$

$$- \int_{r<3.52} \phi^{(4)}_{n'}(\underline{r}-\underline{R}_t)\,U_2(r)\,\phi^{(4)}_{n'}(\underline{r})\,d\tau \qquad (5.42)$$

$$+ \int_{|\underline{r}-\underline{R}_t|<3.52} \left[\phi_{n'}(\underline{r}-\underline{R}_t) - \phi^{(4)}_{n'}(\underline{r}-\underline{R}_t)\right] U_2(r)\,\phi_{n'}(\underline{r})\,d\tau,$$

where the first integral on the right hand side is over all space. The latter integral may easily be evaluated using ellipsoidal co-ordinates [see e.g. Fletcher (1953)] and the two other integrals may be treated in the same way as the integrals $I_t^{(n'n')}$. In the case of the last integral this involves expanding $U_2(r)\phi_{n'}(\underline{r})$ about the second centre and to facilitate this two different fits for P(r) were used, viz. (5.13) and the first two terms of (5.11). Thus $U_2(r)f(r) \simeq r[0.0545\,e^{-0.54r} + 0.455\,e^{-1.144r}$

$$-0.0466\,e^{-0.68r} - 1.004\,e^{-1.147r}]$$

and in this way only the simple formula (5.39) is required for expanding about the second centre. Only the first integral on the right hand side of (5.42) contributes significantly for neighbours more distant than the fourth nearest. Integrals $E_t^{(n'n')}$ calculated

by methods described above for t = 1, ...4 are given in table 9, and the total two-centre contributions $F_t^{(n'n')}$, given by (5.31), are also tabulated for all neighbours up to the ninth nearest neighbours. For t = 5, 6..9 integrals $F_t^{(n'n')}$ and $E_t^{(n'n')}$ are practically equal since the $I_t^{(n'n')}$ are negligible for these more distant neighbours.

Non-orthogonality integrals were treated by exactly similar methods to those described above. Formulae similar to (5.40) were used for first and second nearest neighbours; the radial integrals for $r < 3.52$ were calculated numerically and analytic formulae were used in the regions $3.52 < r < R_t$ and $r > R_t$ as before. For more distant neighbours equation (5.42), with the factors U(r) and $U_2(r)$ omitted, was used for the region $r > 3.52$. Non-orthogonality integrals $S_t^{(n'n')}$ are given in table 10 for t = 1, 2,...9.

The estimated overall accuracy in $F_t^{(n'n')}$ and $S_t^{(n'n')}$ is 5%.

17.3 Evaluation of $J_o^{(nn)}$

It is now convenient to discuss the integral

$$J_o^{(nn)} = \int [\phi_n(\underline{r})]^2 [V(\underline{r}) - U(r)] d\tau \qquad (5.45)$$

which has so far not been considered as it is a very special case. It will be discussed at this point since it involves two-centre integrals which are really degenerate cases of three-centre integrals. For this reason Fletcher (1952) essentially neglected $J_o^{(nn)}$ in his two-centre calculation, treating it as a mere additive constant independent

of n. However, Slater and Koster (1954) and Asdente and Friedel (1961) have included $J_o^{(nn)}$ in their tight-binding calculations.

The potential [V - U] has cubic symmetry and there are two distinct values of $J_o^{(nn)}$, one for the d states of Γ_{25}' symmetry (n = 1, 2, 3) and one for those of Γ_{12} symmetry (n = 4, 5). Integral (5.43) may be written

$$J_o^{(nn)} = -E_o^{(nn)} + \sum_{i \neq o} T_o^{(nn)} \qquad (5.44)$$

where

$$E_o^{(nn)} = \int_{r_o}^{\infty} [P(r)]^2 \, U(r) dr = 0.0541 \text{ ry}$$

and

$$T_{oi}^{(nn)} = \int_{(i)} [\phi(r)]^2 \, U(\underline{r} - \underline{R}_i) d\tau$$

If $\underline{R}_i = R_i(l, m, n)$ relations just like (5.25) exist between $T_{oi}^{(nn)}$ and integrals $T_{oi}^{(n'n')}$ defined by (5.35) with $\underline{R}_t = 0$. The latter integrals were evaluated in a very similar way to that used for the integrals $I_t^{(n'n')}$, $[\phi_n(r)]^2$ being expanded about $\underline{R}_i$. Since $[P(r)]^2$ falls off rapidly as r increases it was only necessary to take i = 1 and 2, corresponding to nearest and next nearest neighbours. The results obtained are as follows:

Nearest neighbours: $T_{01}^{(1'1')} = -5.64 \times 10^{-5}$

$$T_{01}^{(2'2')} = -2.50 \times 10^{-3}$$

$$T_{01}^{(5'5')} = -4.71 \times 10^{-2}$$

Next nearest neighbours:

$$T_{02}^{(1'1')} = -1.87 \times 10^{-6}$$

$$T_{02}^{(2'2')} = -6.35 \times 10^{-5}$$

$$T_{02}^{(5'5')} = -8.31 \times 10^{-4}$$

From (5.44) and the relations between $T_{oi}^{(nn)}$ and $T_{oi}^{(n'n')}$ one finds

$$J_o^{(11)} = -E_o^{(11)} + 5T_{01}^{(1'1')} + 4T_{01}^{(2'2')} + 3T_{01}^{(5'5')} + 2T_{02}^{(1'1')} + 4T_{02}^{(2'2')}$$

$$J_o^{(44)} = -E_o^{(44)} + \frac{9}{2}T_{01}^{(1'1')} + 6T_{01}^{(2'2')} + \frac{3}{2}T_{01}^{(5'5')} + 3T_{02}^{(1'1')} + 3T_{02}^{(5'5')}.$$

Hence it is found that

$$J_o^{(11)} = -0.\not{9}206 \text{ ry} \qquad J_o^{(44)} = -0.185 \text{ ry} \tag{5.45}$$

These results are accurate to within 1%.

The 'cubic field splitting' $J_o^{(44)} - J_o^{(11)}$ of 0.033 ry may be compared with the value 0.046 ry deduced by Slater and Koster (1954) in an application of their interpolation tight-binding method to Howarth's (1953) results on Cu. Cubic field splitting is obtained although the potential in the present calculation is spherically symmetric within each unit cell; it arises from the extension of the atomic d functions into neighbouring cells. This cubic field splitting must be distinguished from that due to departure of the potential from spherical symmetry within a unit cell. Estimates of the latter effect by Leigh (1950) and Callaway and Edwards (1960) show it to be very much smaller (~ 0.05 e.v. in Cu).

17.3 Three-centre integrals

Three-centre integrals have normally been neglected in band structure calculations by the tight-binding method and only Corbato (1956) has included them explicitly in his work on graphite. The reason for this neglect is the extreme difficulty of calculating them, and the standard method of Barnett and Coulson (1951) is very laborious. This method involves expanding both radial wave functions, using formulae such as (5.39), about the potential centre. An infinite series of integrals remains which is often slowly convergent. The inclusion of 49 three-centre integrals in the present calculation was made possible by the introduction of a new method of calculation which, to a good approximation, reduces each three-centre integral to a two-

centre one. This new method will first be described and then the approximation on which it is based will be examined.

In the evaluation of a complicated integral such as (5.35) it is useful to employ simple analytic approximations to the radial wave functions and expressions (5.14) and (5.15) were used. (5.15) was used for wave functions on centres which are nearest neighbours to the potential centre and (5.14) was used for more distant centres. Greater accuracy could, of course, be obtained using two-term fits but the error involved in using (5.14) and (5.15) should not be greater than that involved in the subsequent approximation to be described. Reasonable one-term fits are made possible by the fact that they need only be valid over a sphere of radius r_0.

To illustrate the general method of evaluating three-centre integrals consider the integral

$$T_{ti}^{(1'1')} = \int_{(i)} \phi_{1'}(\underline{r} - \underline{R}_t)\, U(\underline{r} - \underline{R}_1)\phi_{1'}(\underline{r})\,d\tau$$

where $\underline{R}_1$ may be at different distances from the origin than $\underline{R}_t$ so that the fits to the radial wave functions for the two ϕ functions may be different. It is convenient to take the origin at $\underline{R}_1$ so that the integral becomes

$$T_{ti}^{(1'1')} = \int_{(o)} \phi_{1'}(\underline{r} - \underline{R}_2)\, U(\underline{r})\phi_{1'}(\underline{r} - \underline{R}_t)\,d\tau$$

where

$$\underline{R}_1 = -\underline{R}_1 \quad , \quad \underline{R}_2 = -\underline{R}_1 + \underline{R}_t \ .$$

Referred to axes $Ox'y'z'$ the wave function centres C_1 and C_2 in figure 15 have the same x' and y' co-ordinates since Oz' is parallel to C_1C_2. Thus the components of $\underline{R}_1$ and $\underline{R}_2$ referred these axes may be written

$$\underline{R}_1 = (X', Y', Z_1')$$

$$\underline{R}_2 = (X', Y', Z_2') \ .$$

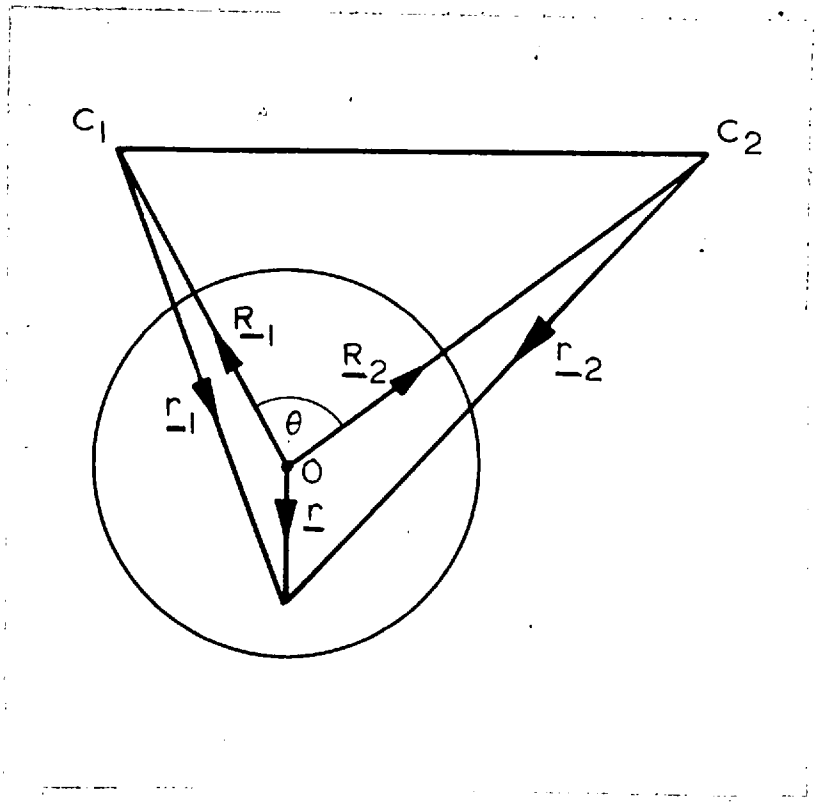

Fig. 15

Suppose

$$\phi_{1'}(\underline{r} - \underline{R}_1) = A_1(x' - X')(y' - Y') \exp(-\alpha_1 r_1)$$

$$\phi_{1'}(\underline{r} - \underline{R}_2) = A_2(x' - X')(y' - Y') \exp(-\alpha_2 r_2)$$

where $\underline{r}_1 = \underline{r} - \underline{R}_1$ and $\underline{r}_2 = \underline{r} - \underline{R}_2$, so that

$$T_{ii}^{(1'1')} = A_1 A_2 \int_{(o)} (x'-X')^2 (y'-Y')^2 e^{-\alpha_1 r_1 - \alpha_2 r_2} U(r)\, d\tau. \qquad (5.46)$$

When the approximations (5.14) and (5.15) are used α_1 and α_2 take values 0.85 or 1.1. The difficulty in evaluating (5.46) is that of expressing the exponential term in terms of co-ordinates referred to O. The idea behind the method used is to exploit the fact that over the sphere surrounding the origin the main variation of $e^{-\alpha_1 r_1}$ is in the direction of the vector $\underline{R}_1$, and similarly for $e^{-\alpha_2 r_2}$. Thus to a first approximation

$$\begin{aligned} e^{-\alpha_1 r_1 - \alpha_2 r_2} &\simeq \exp\left(\alpha_1 \frac{\underline{r}_1 \cdot \underline{R}_1}{R_1} + \alpha_2 \frac{\underline{r}_2 \cdot \underline{R}_2}{R_2}\right) \\ &= \exp\left\{-\alpha_1\left(R_1 - \frac{\underline{r} \cdot \underline{R}_1}{R_1}\right)\right. \\ &\qquad \left. - \alpha_2\left(R_2 - \frac{\underline{r} \cdot \underline{R}_2}{R_2}\right)\right\}. \end{aligned} \qquad (5.47)$$

If

$$\gamma \underline{\lambda} = \frac{\alpha_1}{R_1} \underline{R}_1 + \frac{\alpha_2}{R_2} \underline{R}_2 , \qquad (5.48)$$

where $\underline{i}$ is a unit vector, (5.47) may be put in the form

$$e^{-\alpha_1 r_1 - \alpha_2 r_2} \simeq \exp\left[\gamma(-\underline{R} + \underline{r}).\underline{i}\right], \qquad (5.49)$$

where

$$\underline{R} = \frac{\alpha_1 R_1 + \alpha_2 R_2}{\gamma}\,\underline{i} = \frac{\alpha_1 R_1 + \alpha_2 R_2}{\gamma^2}\left(\frac{\alpha_1}{R_1}\underline{R}_1 + \frac{\alpha_2}{R_2}\underline{R}_2\right). \qquad (5.50)$$

γ, defined by (5.48), may be expressed as

$$\gamma = \left(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2 \cos\theta\right)^{1/2} \qquad (5.51)$$

where θ is the angle between $\underline{R}_1$ and $\underline{R}_2$.

The original approximation may be used the other way round on (5.49) so that

$$e^{-\alpha_1 r_1 - \alpha_2 r_2} \simeq e^{-\gamma|\underline{r} - \underline{R}|}. \qquad (5.52)$$

When this approximation is used in (5.46) the three-centre integral is reduced to a two-centre integral, the centres being the origin and the point $\underline{R}$ defined by (5.50). Thus

$$T_{ti}^{(ii')} \simeq A_1 A_2 \int_{(o)} (x'-X')^2 (y'-Y')^2 e^{-\gamma|\underline{r} - \underline{R}|} U(r)\, d\tau \qquad (5.53)$$

and the exponential may be expanded about the origin as in the

method of Barnett and Coulson (1951). The evaluation of (5.53) will not be described in detail as the method is very similar to that previously described for two-centre integrals. The radial integrals which appear were calculated analytically using expressions (5.4) for U(r).

It is now necessary to examine the accuracy of the approximation (5.52). This approximation may be obtained as the first term in a series for $e^{-\alpha_1 r_1 - \alpha_2 r_2}$ and the next term in the series will now be derived. Consider first the following expression for $e^{-\alpha_1 r_1}$,

$$\begin{aligned} e^{-\alpha_1 r_1} &= \exp\left[-\alpha_1 \left(R_1^2 + r^2 - 2\underline{R}_1 . \underline{r}\right)^{\frac{1}{2}}\right] \\ &= \exp\left[-\alpha_1 \left\{\left(R_1 - \frac{\underline{R}_1 . \underline{r}}{R_1}\right)^2 + r^2 - \left(\frac{\underline{R}_1 . \underline{r}}{R_1}\right)^2\right\}^{\frac{1}{2}}\right] \\ &= \exp\left[-\alpha_1 \left(R_1 - \frac{\underline{r} . \underline{R}_1}{R_1}\right)\left\{1 + \frac{r^2 - \left(\frac{\underline{r} . \underline{R}_1}{R_1}\right)^2}{\left(R_1 - \frac{\underline{r} . \underline{R}_1}{R_1}\right)^2}\right\}^{\frac{1}{2}}\right] \end{aligned} \tag{5.54}$$

It is not difficult to show that

$$\frac{r^2 - \left(\frac{\underline{r} . \underline{R}_1}{R_1}\right)^2}{\left(R_1 - \frac{\underline{r} . \underline{R}_1}{R_1}\right)^2} \leqslant \frac{r^2}{R_1^2 - r^2} \leqslant \frac{1}{3} \tag{5.55}$$

since $r \leqslant \frac{1}{2}R_1$. The expression raised to the power $\frac{1}{2}$ in (5.54)

may therefore be expanded in a binomial series which may be terminated at the second term to a good approximation. The third term is always less than (1/72). Thus

$$e^{-\alpha_1 r_1} = \exp\left[-\alpha_1\left(R_1 - \frac{\underline{r}\cdot\underline{R}_1}{R_1}\right) - \frac{\alpha_1}{2}\,\frac{r^2 - \left(\frac{\underline{r}\cdot\underline{R}_1}{R_1}\right)^2}{R_1 - \frac{\underline{r}\cdot\underline{R}_1}{R_1}} \cdots\right]$$

and similar expressions hold for $e^{-\alpha_2 r_2}$ and $e^{-\gamma|\underline{r}-\underline{R}|}$ (Inequality (5.55) holds in the latter case since in all cases which have been evaluated $R > 2r_0$). It is now straightforward to show that

$$e^{-\alpha_1 r_1 - \alpha_2 r_2} = e^{-\gamma|\underline{r}-\underline{R}|}\exp\left\{\frac{\gamma}{2}\cdot\frac{r^2 - \left(\frac{\underline{r}\cdot\underline{R}}{R}\right)^2}{R - \frac{\underline{r}\cdot\underline{R}}{R}} - \frac{\alpha_1}{2}\cdot\frac{r^2 - \left(\frac{\underline{r}\cdot\underline{R}_1}{R_1}\right)^2}{R_1 - \frac{\underline{r}\cdot\underline{R}_1}{R_1}} - \frac{\alpha_2}{2}\cdot\frac{r^2 - \left(\frac{\underline{r}\cdot\underline{R}_2}{R_2}\right)^2}{R_2 - \frac{\underline{r}\cdot\underline{R}_2}{R_2}} \cdots\right\}$$

If the expression in curly brackets is represented by δ

$$e^{-\alpha_1 r_1 - \alpha_2 r_2} = e^{-\gamma|\underline{r}-\underline{R}|}\left\{1 + \delta + \frac{\delta^2}{2} + \cdots\right\}. \qquad (5.56)$$

Since δ appears to be always negative and, even for $r = r_0$ in the

worst case considered, $|\delta| \lesssim 1.5$ the successive correction terms in (5.56) decrease and alternate in sign. An overestimate of the error must therefore be obtained by examining the δ term only. The denominators in δ may be expanded in binomial series and the leading term δ_0 takes the form

$$\delta_0 = \frac{\gamma}{2R}\left\{r^2 - \left(\frac{\underline{r}\cdot\underline{R}}{R}\right)^2\right\} - \frac{\alpha_1}{2R_1}\left\{r^2 - \left(\frac{\underline{r}\cdot\underline{R}_1}{R_1}\right)^2\right\}$$

$$- \frac{\alpha_2}{2R_2}\left\{r^2 - \left(\frac{\underline{r}\cdot\underline{R}_2}{R_2}\right)^2\right\}.$$

On substituting for γ and $\underline{R}$ from (5.50) and (5.51) one obtains

$$\delta_0 = \frac{r^2}{2}\left\{\frac{\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2\cos\theta}{\alpha_1 R_1 + \alpha_2 R_2} - \frac{\alpha_1}{R_1} - \frac{\alpha_2}{R_2}\right\}$$

$$-\frac{1}{2}\left\{\frac{1}{\alpha_1 R_1 + \alpha_2 R_2}\left[\alpha_1\frac{\underline{r}\cdot\underline{R}_1}{R_1} + \alpha_2\frac{\underline{r}\cdot\underline{R}_2}{R_2}\right]^2 - \frac{\alpha_1}{R_1}\left(\frac{\underline{r}\cdot\underline{R}_1}{R_1}\right)^2 - \frac{\alpha_2}{R_2}\left(\frac{\underline{r}\cdot\underline{R}_2}{R_2}\right)^2\right\}$$

which simplifies to

$$\delta_0 = -\frac{\alpha_1\alpha_2 r^2}{2R_1R_2(\alpha_1R_1 + \alpha_2R_2)}(\underline{R}_1 - \underline{R}_2)^2$$

$$+\frac{\alpha_1\alpha_2}{2(\alpha_1R_1 + \alpha_2R_2)}\left\{\underline{r}\cdot\left[\sqrt{\frac{R_2}{R_1}}\frac{\underline{R}_1}{R_1} - \sqrt{\frac{R_1}{R_2}}\frac{\underline{R}_2}{R_2}\right]\right\}^2.$$

If $\underline{j}$ is a unit vector in the direction of

$$\sqrt{\frac{R_2}{R_1}}\,\frac{\underline{R}_1}{R_1} - \sqrt{\frac{R_1}{R_2}}\,\frac{\underline{R}_2}{R_2} \,,$$

ψ is the angle between $\underline{r}$ and $\underline{j}$ and $\rho = c_1 c_2$,

$$\delta_0 = -\frac{\alpha_1 \alpha_2 \rho^2}{2R_1R_2(\alpha_1 R_1 + \alpha_2 R_2)}\, r^2 \sin^2\psi \,. \qquad (5.57)$$

In the case when $\alpha_1 = \alpha_2 = \alpha$ and $R_1 = R_2 = R$, $\underline{j}$ is in the direction of $\underline{R}_1 - \underline{R}_2$ and is perpendicular to $\underline{i}$. An estimate of the fractional error in using approximation (5.52) to evaluate the integral (5.46) in such a case may be made as follows. In making this estimate the polynomial terms in the integrand which arise from the angular parts of wave functions not centred at the origin, will be omitted as they are slowly-varying compared with the exponential term. It is also convenient to use approximation (5.49) for the exponential term and, in the notation of fig.16 the approximate fractional error in (5.46) may be written

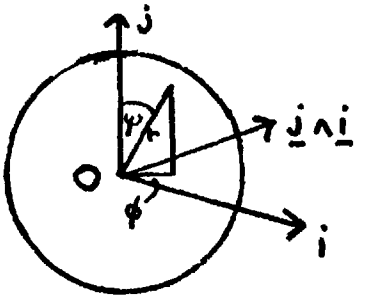

Fig. 16

$$\epsilon = \langle \delta_0 \rangle = \frac{\iiint_{(o)} \delta_0 \exp(\gamma r \sin\psi \cos\phi)\, U(r)\, r^2 \sin\psi \, dr d\psi d\phi}{\iiint_{(o)} \exp(\gamma r \sin\psi \cos\phi)\, U(r)\, r^2 \sin\psi \, dr d\psi d\phi}$$

$$= -\frac{\alpha \rho^2}{4R^3} \langle r^2 \sin^2\psi \rangle \qquad (5.58)$$

Using the following formulae [Watson (1944)]

$$\int_0^{2\pi} e^{z\cos\phi} \, d\phi = 2\pi I_0(z)$$

$$\int_0^{\pi/2} I_0(z \sin\psi) \sin\psi \cos^2\psi \, d\psi = \frac{2^{\frac{1}{2}} \Gamma(\frac{3}{2})}{z^{3/2}} I_{\frac{3}{2}}(z)$$

it is straightforward to show that

$$\langle r^2 \sin^2\psi \rangle = \frac{1}{\gamma^2} + \frac{\int_0^{r_0} r^2 U(r) \left[r \sinh\gamma r - \frac{1}{\gamma} \cosh\gamma r \right] dr}{\int_0^{r_0} r\, U(r) \sinh\gamma r \, dr}$$

and the radial integrals are easily evaluated using expressions (5.4) for U(r). In the important case when the two wave function

centres and the potential centre are all nearest neighbours of each other the appropriate γ_λ is given by (5.31) with $\alpha_1 = \alpha_2 = 1.1$ (using fit (5.15) for P) and $\theta = \pi/3$. Thus $\gamma = 1.9055$ and it is found that $\langle r^2 \sin^2\psi \rangle = 1.76$. From (5.58) with $\rho = R = 4.82$ one finds $\epsilon = 0.078$. It has already been pointed out that the error term considered must over estimate the error which in this case is probably considerably less than 7.8%. It is very unlikely that in any three-centre integral which has been calculated the error exceeds 10%. The calculation of the three-centre integrals is the greatest source of error in the present work but the error involved is regarded as just tolerable in a calculation of this complexity.

The new method of calculating three-centre integrals which has been described may be generally useful in cases when great accuracy is not required. Such would be the case, for example, even in quite an accurate calculation, when the three-centre integrals were small and represented a minor correction to a two centre approximation.

The method described above was used to calculate 49 three-centre integrals which contribute to $G_t^{(n'm')}$ $t = 1 \ldots 4$. The values obtained are given in tables 11, 12, 13 and 14. It was not necessary to calculate each three-centre integral individually since they occur in groups of 1, 2, 4 or 8 equal integrals as indicated in the tables.

Thus, for example, the four integrals

$$\int_{(i)} \phi_{n'}(\underline{r} - \underline{R}_j)\, U(\underline{r} - \underline{R}_i)\, \phi_{m'}(\underline{r})\, d\tau,$$

where $\underline{R}_i$ is a nearest neighbour of both the origin and $\underline{R}_j$, are all equal as is readily shown by making the replacements $x' \rightarrow \pm x'$, $y' \rightarrow \pm y'$ in the integration variables. These form the group of integrals (i) in table 11. The convenience of considering the three-centre integrals in groups of equal integrals is the reason for expressing the original energy integrals $J_t^{(nm)}$ in terms of the integrals $J_t^{(n'm')}$. In the case of the nearest neighbour energy integrals it is certain that sufficient three-centre integrals have been included for convergence. For 2nd, 3rd and 4th nearest neighbour integrals it is not quite certain that all three-centre integrals neglected are in fact negligible. However, their inclusion would be unlikely to lead to any substantial improvement in the final result.

The three-centre contributions $\epsilon_t^{(n'm')}$, $t = 5, \ldots, 9$, were estimated by a much simpler method than that described above. For

t greater than 4 the two-centre integrals

$$T_{to}^{(n'm')} = T_{tt}^{(n'm')} = I_t^{(n'n')} \delta_{n'm'}$$

are negligible so that to an excellent approximation

$$C_t^{(n'm')} = \int \phi_{n'}(\underline{r} - \underline{R}_t)\, V(\underline{r})\, \phi_{m'}(\underline{r}) d\tau .$$

For sufficiently large t, when a very large number of unit cells make a significant contribution, it must be a good approximation to replace $V(\underline{r})$ by its average value $\bar{V}$. Hence for large t

$$C_t^{(n'm')} \simeq \bar{V} \quad S_t^{(n'm')} .$$

This approximation is a very convenient one to use in estimating the contribution of three-centre integrals to energy integrals in which the wave functions are centred on sites more distant than fourth nearest neighbours. The validity of the approximation may be checked in the case of fourth nearest neighbours where it would not be expected to be too accurate. $\bar{V}$ is easily calculated by averaging over a unit cell so that

$$\bar{V} = \frac{4}{a^3} \int_0^{r_0} U(r) . 4\pi r^2 dr = -1.57$$

A comparison between $J_4^{(n'm')}$ and $-1.57\, S_4^{(n'm')}$ is given below:

	(1'1')	(2'2')	(3'3')	(4'4')	(5'5')	(4'5')
$J_4^{(n'm')} \times 10^3$	-1.77	3.93	2.85	-0.495	-4.94	0.085
$-1.57 S_4^{(n'm')} \times 10^3$	-0.837	3.47	3.47	-0.837	-3.44	0

The agreement is not good but it should be better for more distant neighbours. $J_t^{(n'm')}$ has been taken as

$$J_t^{(n'm')} = [J_t^{(n'n')} - 1.57\, S_t^{(n'n')}]\, \delta_{n'm'} \qquad (5.59)$$

for $t \geq 5$. Values of $J_t^{(n'm')}$, as calculated from (5.30) and tables 9, 11, 12, 13 and 14 for $t = 1, 2 \ldots 4$ and from (5.59) and tables 9 and 10 for $t = 5, 6 \ldots 9$, are given in table 15.

18. Results and Discussion

The final stage in the calculation is to use the integrals $J_t^{(n'm')}$ and $S_t^{(n'm')}$ which have been calculated, to obtain the integrals $J_{(pqr)}^{(nn)}$ which appear in (5.18), (5.19) and the $S_{(pqr)}^{(nn)}$ which appear in corresponding formulae for non-orthogonality integrals. This is easily accomplished for n = 1, 4 and 5 by using formulae of the types (5.25) and (5.28).

The coefficients required have been listed in tables 2, 6, 7 and 8 for neighbours up to fourth nearest. For more distant neighbours

formulae of the form (5.25) apply to both non-orthogonality and energy integrals, since the latter were calculated effectively by a two-centre approximation. The coefficient in (5.25) for those more distant neighbours have not been listed but are easily calculated. Integrals $J^{(22)}_{(pqr)}$ and $S^{(22)}_{(pqr)}$ are found immediately using (5.20). It is not worthwhile tabulating all the integrals obtained and only the result of inserting them in expressions (5.18) and (5.19) will be given.

18.1 Results

The most complete results, calculated up to 9th nearest neighbours, are obtained by adding expressions (5.18) and (5.19). It is convenient to use the notation

$$\epsilon_{nn} = \sum J_t^{(nn)} e^{-i \underline{k} \cdot \underline{R}_t}$$

$$\Delta_{nn} = \sum S_t^{(nn)} e^{-i \underline{k} \cdot \underline{R}_t} ,$$

and the results are as follows.

$$10\,\epsilon_{11} = 0.70 + 1.00 \cos\gamma - 0.65 \cos 2\gamma + 0.13 \cos 3\gamma - 0.03 \cos 4\gamma$$

$$10\,\epsilon_{22} = 2.04 - 3.68 \cos\gamma + 1.19 \cos 2\gamma + 0.32 \cos 3\gamma + 0.36 \cos 4\gamma$$

$$10\,\epsilon_{44} = 0.99 - 0.74 \cos\gamma + 0.48 \cos 2\gamma - 0.05 \cos 3\gamma - 0.03 \cos 4\gamma$$

$$10\,\epsilon_{55} = -8.11 + 4.86 \cos\gamma + 5.26 \cos 2\gamma - 0.48 \cos 3\gamma - 0.86 \cos 4\gamma$$

(5.60

$$10\,\Delta_{11} = 10.33 - 1.41\cos\gamma + 0.32\cos 2\gamma - 0.05\cos 3\gamma + 0.02\cos 4\gamma$$

$$10\,\Delta_{22} = 6.51 + 1.24\cos\gamma - 0.17\cos 2\gamma - 0.12\cos 3\gamma - 0.15\cos 4\gamma$$

$$10\,\Delta_{44} = 7.59 + 0.16\cos\gamma - 0.10\cos 2\gamma + 0.01\cos 3\gamma + 0.01\cos 4\gamma$$

$$10\,\Delta_{55} = 14.07 - 4.27\cos\gamma - 2.74\cos 2\gamma + 0.25\cos 3\gamma + 0.59\cos 4\gamma \qquad (5.61)$$

The corresponding expressions calculated only up to 4th nearest neighbours are as follows:

$$10\,\epsilon_{11} = 0.13 + 0.15\cos\gamma - 0.18\cos 2\gamma$$

$$10\,\epsilon_{22} = 0.87 - 3.21\cos\gamma + 2.44\cos 2\gamma$$

$$10\,\epsilon_{44} = 1.82 + 0.42\cos\gamma - 0.27\cos 2\gamma$$

$$10\,\epsilon_{55} = -3.72 + 5.46\cos\gamma + 3.24\cos 2\gamma \qquad (5.62)$$

$$10\,\Delta_{11} = 10.65 - 1.04\cos\gamma - 0.08\cos 2\gamma$$

$$10\,\Delta_{22} = 6.85 + 1.42\cos\gamma - 0.74\cos 2\gamma$$

$$10\,\Delta_{44} = 7.19 - 0.38\cos\gamma + 0.24\cos 2\gamma$$

$$10\,\Delta_{55} = 13.44 - 4.55\cos\gamma - 1.04\cos 2\gamma \qquad (5.63)$$

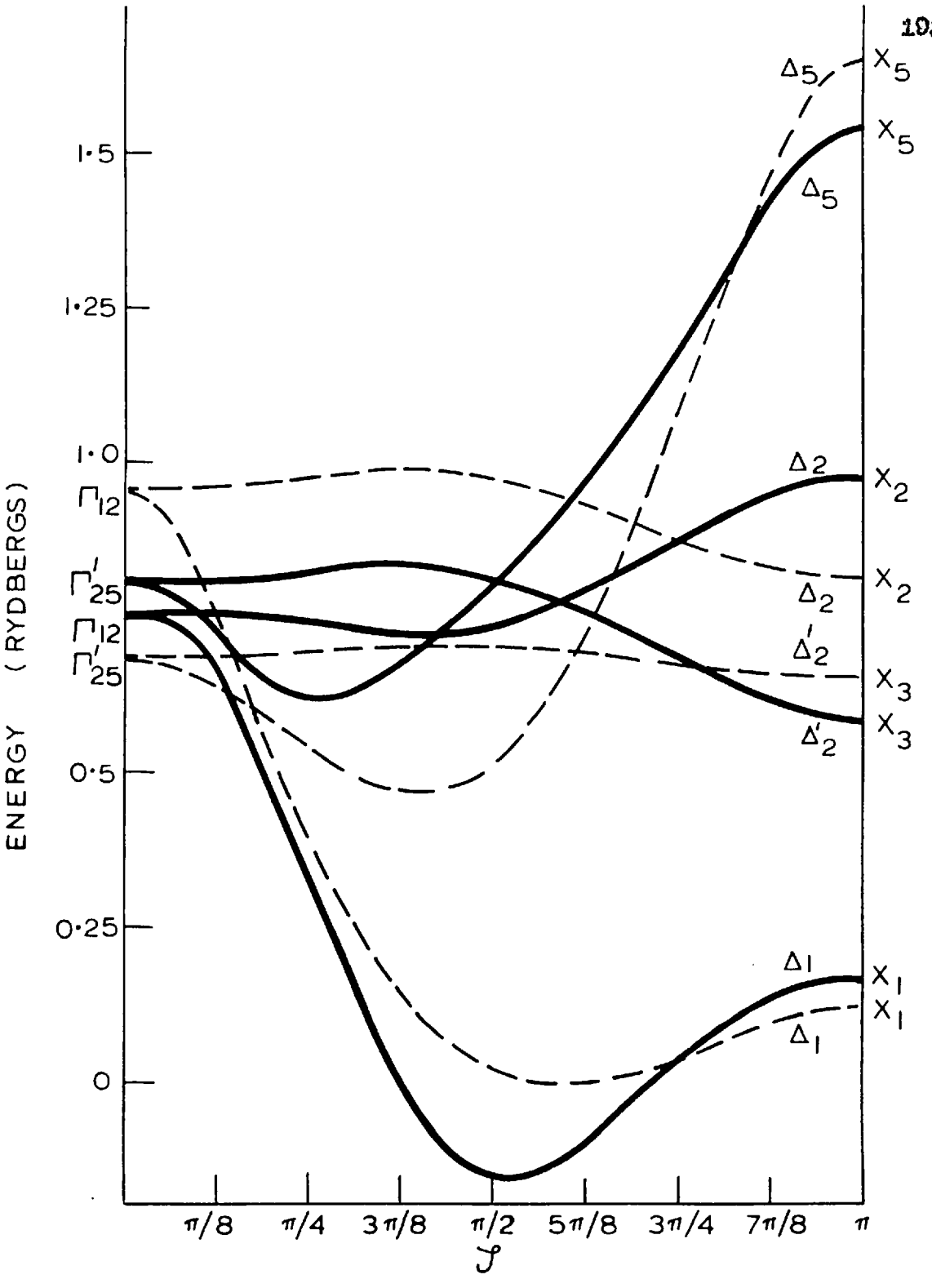

FIGURE **17:** Energy bands in the (001) direction. The broken and solid curves were calculated by including all energy and non-orthogonality integrals up to 4th and 9th nearest neighbours respectively.

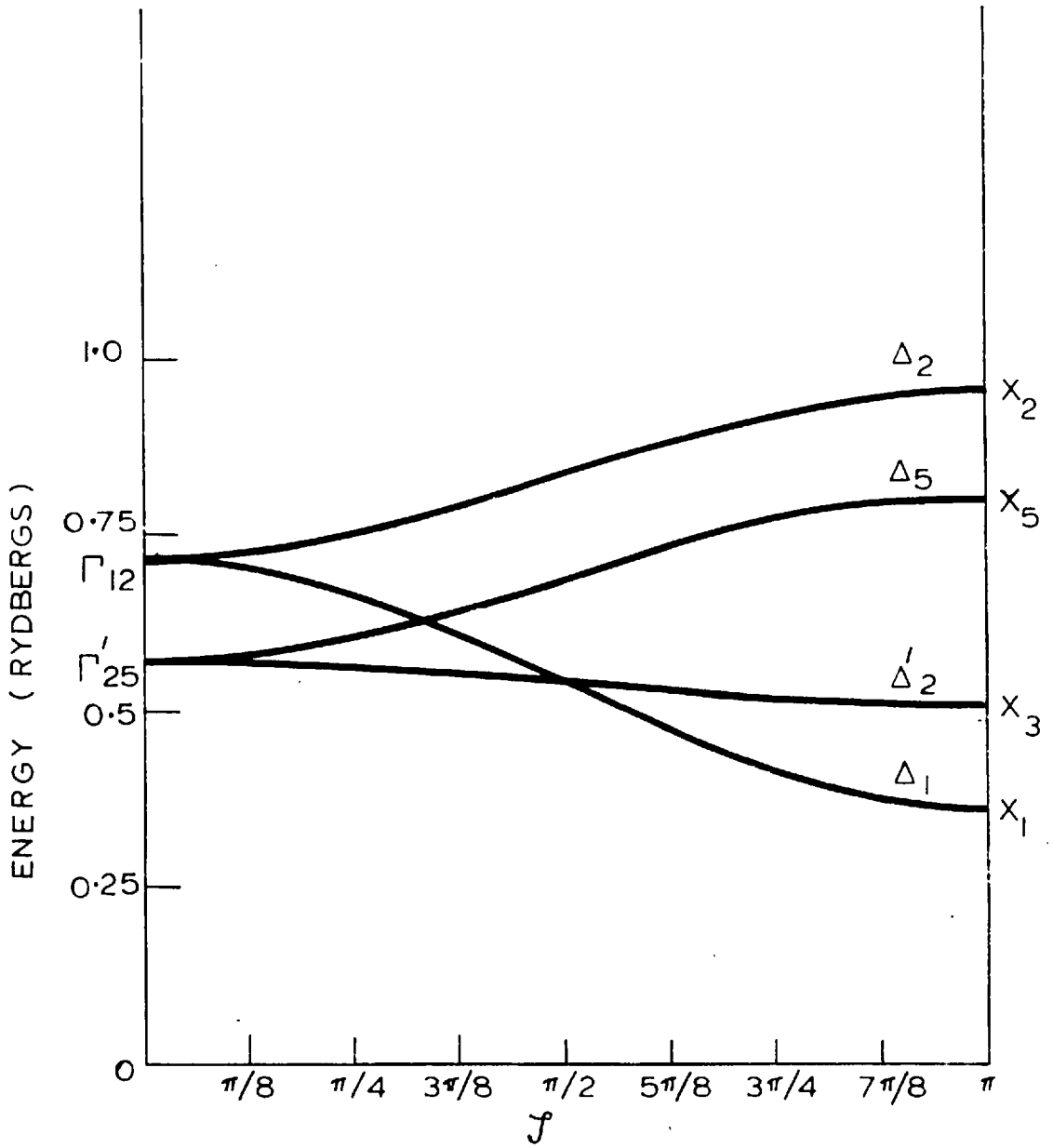

FIGURE 18: Energy bands in the (001) direction calculated with the two-centre nearest neighbour approximation.

The four distinct energy bands (E_2 is doubly degenerate) for $\underline{k} = (0, 0, 2\gamma/a)$ are given by (5.16) as

$$E_n(\underline{k}) = E_0 + (\epsilon_{nn}/\Delta_{nn}) \quad , n = 1, 2, 4, 5.$$

The results are plotted in figure 17 for the case when only integrals up to fourth nearest neighbours are included as well as the case when all integrals up to ninth nearest neighbours are included. The notation of Bouckaert, Smoluchowski and Wigner (1936) is used to label the curves and the representation to which each Bloch function belongs was indicated in section 15. The energies calculated within the two-centre nearest neighbour approximation ~~(i.e. Slater-Koster approximation)~~ are

$$E_1 = 0.540 + 0.080 \cos\gamma$$

$$E_2 = 0.688 - 0.118 \cos\gamma$$

$$E_4 = 0.835 - 0.118 \cos\gamma$$

$$E_5 = 0.541 + 0.176 \cos\gamma$$

These are plotted in figure 18. All energies in the figures are referred to the zero of energy between 'muffin-tin' spheres.

18.2 Discussion

It was originally intended to compare the results of this calculation with those of Howarth (1955) which were calculated with the same crystal potential. However, it has already been mentioned that this APW calculation of Howarth's is now regarded as inaccurate. Since

recent work (Segall 1962) indicates that the d band is not so sensitive to the crystal potential as was once thought, it is not unreasonable to attempt a comparison with Howarth's earlier calculation (1953) by the cellular method. The potential within the cell is identical with that within the inscribed sphere in the APW calculation and the difference in crystal potential outside spheres should only have a small effect on the d band. A glance at figure 17 shows that in fact no real comparison with the present calculation is possible. The width of the d band in Howarth's calculation is 0.256ry whereas in the present calculation it is 1.30 ry. The tight-binding method has clearly broken down and, as discussed in Chapter 4, the reason is the use of the natural choice of 'atomic' potential which leads to 'atomic' functions which are too diffuse. The error incurred through using these functions is not larger than an upper bound estimate obtained by the method of section 8.3, which was applied to d bands in section 12.1. The upper bound is given by (8.3) and it was pointed out that the main contribution to the integral comes from the immediate vicinity of the nearest neighbour sites. The error is thus roughly proportional to $|\phi(r)|^2$ evaluated at these sites. At the nearest neighbour distance the radial 'atomic' function used in the present calculation is seven times as large as the Hartree-Fock Cu^+ function. Thus the error might be expected to be about 50 times larger than the 0.04 rydbergs estimate of section 12.1. This gives an upper bound to

the error of 2 rydbergs, so that the errors actually obtained are not surprising.

It is seen from figure 18 that the width of the d band in the two-centre nearest neighbour approximation is 0.60 ry. It must be admitted that an initial calculation of this width led to an erroneous value only half as big. This was sufficiently encouraging to justify proceeding with the calculation of three-centre integrals etc. These then seemed to have an overwhelming effect on the band width in view of its apparently small value within the simple approximation. This effect does not now seem so surprisingly large, but nevertheless it is mainly due to the inclusion of three-centre integrals that the band width in figure 17 is three times that in figure 18 .

Comparison of the two sets of curves in figure shows that, even when 9th nearest neighbour integrals are included, it is not certain whether stable E(k) curves have been obtained. The difference between the curves obtained in the 4th nearest neighbour approximation and the 9th nearest neighbour approximation are small compared with the calculated band width, but nevertheless big enough to invert the Γ_{12} and Γ'_{25} levels. To ensure that convergence has been achieved in the 9th nearest neighbour approximation one would have to proceed to the 13th nearest neighbour approximation, say, and make a further comparison. It appears that, with 'atomic' functions as diffuse as the present ones,

the tight-binding method is not only inaccurate but hardly practicable. Certainly all its attractive simplicity has been lost.

Some features of the curves in figure 17 can be explained by the fact that the trial functions are not exactly orthogonal to the core functions. It was pointed out in section 6.3 that this non-orthogonality arises through overlap of the 'atomic' functions with core functions on neighbouring sites. This effect must be particularly marked in the present case since the 'atomic' functions are rather extended. Core states are of s and p symmetries and reference to tables in Chapter 3 of Jones' (1960) book shows that they belong to the representations X_1, Δ_1 and Δ_5, among others. States of these symmetries calculated by the tight-binding method, which is variational in character, need not necessarily lie above the true eigenvalues. On the other hand, if the tight-binding method has been rigorously pursued, states of Γ_{12}, Γ_{25}', X_2, X_3, X_5, Δ_2 and Δ_2' symmetries must lie above the true eigenvalues. These observations probably account for the low X_1 level in figure 17 and the sagging Δ_1 and Δ_5 curves. The X_1 level is dragged down by mixing with 3s core functions and points on the Δ_1 curve can be depressed still further by mixing with both 3s and 3p core functions. The Δ_5 curve sags through mixing with the 3p core functions whilst for its end points, Γ_{25}' and X_5, no such mixing is possible.

A check on the rigour with which the tight-binding method has been pursued here may be made by verifying that those levels which are

automatically orthogonal to the core do in fact lie above the accurately calculated eigenvalues. Howarth's (1953) values, although calculated for a slightly different potential, should be quite accurate and a comparison with these will now be made. [Segall (1962) estimates the energy shifts of levels in going from a 'muffin-tin' potential to a potential which is close to a cellular potential as less than 0.005 ry.] Howarth's values given below are adjusted to the same zero of potential as the tight-binding results. The latter results are for the 9th nearest neighbour approximation.

State	Present Calculation	Howarth
Γ_{12}	0.76	0.756
Γ_{25}'	0.81	0.696
X_1	0.16	0.81
X_2	0.98	0.80
X_3	0.59	0.587
X_5	1.54	0.843

It is gratifying to note that all states except X_1 lie above the accurate eigenvalues. This suggests that the 9th nearest neighbour approximation includes enough integrals for convergence. It is seen from figures 17 and 18 that with the nearest neighbour and 4th nearest neighbour approximations some states lie below their correct values.

It is surprising how accurate some of the eigenvalues are. Apart

from the X_5 level (ignoring the X_1 level which is expected to be inaccurate) the errors are all an order of magnitude smaller than the upper bound estimate of 2 rydbergs. This augurs well for better controlled tight-binding calculations along the lines indicated in Chapter 4.

Table 1 : Values of the potential $v_o(r)$ in rydberrs

r	$v_o(r)$	r	$v_o(r)$	r	$v_o(r)$
0.005	11334.0	0.52	29.150	2.12	1.1687
0.010	5538.0	0.56	24.638	2.16	1.1280
0.015	3611.0	0.60	21.320	2.20	1.0902
0.020	2650.0	0.64	18.411	2.24	1.0550
0.025	2076.0	0.68	15.990	2.28	1.0225
0.030	1696.0	0.72	13.967	2.32	0.99208
0.035	1435.8	0.76	12.275	2.36	0.96359
0.040	1234.4	0.80	10.847	2.40	0.93705
0.045	1068.7	0.84	9.6583	2.44	0.91248
0.050	944.88	0.88	8.6059	2.48	0.88962
0.055	844.25			2.52	0.86826
0.060	760.82	0.92	7.7221	2.56	0.84829
0.065	690.57	0.96	6.9057	2.60	0.82965
0.070	630.78	1.00	6.5074		
0.075	579.16	1.04	5.7562		
0.080	534.24	1.08	5.2586	2.80	0.75250
0.085	494.78	1.12	4.8019	3.00	0.69133
0.090	459.69	1.16	4.4177	3.20	0.64093
0.095	428.98	1.20	4.0765	3.40	0.59833
0.100	401.09	1.24	3.7738	3.60	0.56222
		1.28	3.5033	3.80	0.53035
0.11	353.50			4.00	0.50278
0.12	314.32	1.32	3.2606		
0.13	281.60	1.36	3.0420		
0.14	253.94	1.40	2.8455		
0.15	230.34	1.44	2.6686		
0.16	210.00	1.48	2.5072		
0.17	192.34	1.52	2.3602		
0.18	176.91	1.56	2.2264		
0.19	163.32	1.60	2.1041		
0.20	151.30	1.64	1.9923		
		1.68	1.8888		
0.22	131.03				
0.24	114.66	1.72	1.7944		
0.26	101.20	1.76	1.7077		
0.28	89.955	1.80	1.6278		
0.30	80.459	1.84	1.5532		
0.32	72.288	1.88	1.4854		
0.36	59.074	1.92	1.4220		
0.40	48.877	1.96	1.3637		
0.44	40.819	2.00	1.3091		
0.48	34.356	2.04	1.2589		
		2.08	1.2118		

Table 2: Coefficients of $S_t^{(n'n')}$ in formulae (5.25) for $S_{tu}^{(mn)}$

		$S_t^{(1'1')}$	$S_t^{(2'2')}$	$S_t^{(5'5')}$
$\underline{R}_{tu} = a(\frac{1}{2}, 0, \frac{1}{2})$ and $a(0, \frac{1}{2}, \frac{1}{2})$	$S_{1u}^{(11)}$	$\frac{1}{2}$	$\frac{1}{2}$	0
	$S_{1u}^{(44)}$	$\frac{9}{16}$	$\frac{1}{4}$	$\frac{3}{16}$
	$S_{1u}^{(55)}$	$\frac{3}{16}$	$\frac{3}{4}$	$\frac{1}{16}$
$\underline{R}_{tu} = a(\frac{1}{2}, \frac{1}{2}, 0)$	$S_{1u}^{(11)}$	$\frac{1}{4}$	0	$\frac{3}{4}$
	$S_{1u}^{(44)}$	0	1	0
	$S_{1u}^{(55)}$	$\frac{3}{4}$	0	$\frac{1}{4}$
$\underline{R}_{tu} = a(1, 0, 0)$ and $a(0, 1, 0)$	$S_{2u}^{(11)}$	0	1	0
	$S_{2u}^{(44)}$	$\frac{1}{4}$	0	$\frac{3}{4}$
	$S_{2u}^{(55)}$	$\frac{3}{4}$	0	$\frac{1}{4}$

Table 2 (continued)

		$S_t^{(1'1')}$	$S_t^{(2'2')}$	$S_t^{(5'5')}$
$R_{tu} = a(0, 0, 1)$	$S_{2u}^{(11)}$	1	0	0
	$S_{2u}^{(44)}$	1	0	0
	$S_{2u}^{(55)}$	0	0	1
$R_{tu} = a(1, \frac{1}{2}, \frac{1}{2})$ and $a(\frac{1}{2}, 1, \frac{1}{2})$	$S_{3u}^{(11)}$	$\frac{5}{18}$	$\frac{7}{18}$	$\frac{1}{3}$
	$S_{3u}^{(44)}$	$\frac{11}{48}$	$\frac{7}{12}$	$\frac{5}{16}$
	$S_{3u}^{(55)}$	$\frac{25}{48}$	$\frac{5}{12}$	$\frac{1}{16}$
$R_{tu} = a(\frac{1}{2}, \frac{1}{2}, 1)$	$S_{3u}^{(11)}$	$\frac{25}{36}$	$\frac{2}{9}$	$\frac{1}{12}$
	$S_{3u}^{(44)}$	$\frac{2}{5}$	$\frac{1}{3}$	0
	$S_{3u}^{(55)}$	$\frac{1}{12}$	$\frac{2}{3}$	$\frac{1}{4}$

Coefficients for 4th nearest neighbours a(1, 0, 1), a(0, 1, 1) and a(1, 1, 0) are the same as for corresponding nearest neighbours

Table 3: Character Table for Group of Axis in Nearest Neighbour Direction

	x'y'z'	$\bar{x}$'y'z'	x'$\bar{y}$'z'	$\bar{x}$'$\bar{y}$'z'	Type of d-function
Σ_1	1	1	1	1	$(3z'^2 - r^2)$;$(x'^2 - y'^2)$
Σ_2	1	1	-1	-1	y'z'
Σ_3	1	-1	-1	1	x'y'
Σ_4	1	-1	1	-1	z'x'

Table 4: Character Table for Group of Axis in Next Nearest Neighbour Direction (cubic axis)

	$x'y'z'$	$\bar{x}'\bar{y}'z'$	$y'\bar{x}'z'$ $\bar{y}'x'z'$	$x'\bar{y}'z'$ $\bar{x}'y'z'$	$\bar{y}'\bar{x}'z'$ $y'x'z'$	Types of d-function
Δ_1	1	1	1	1	1	$3z'^2 - r^2$
Δ_2	1	1	-1	1	-1	$x'^2 - y'^2$
Δ_2'	1	1	-1	-1	1	$x'y'$
Δ_1'	1	1	-1	-1	-1	-
Δ_5	2	-2	0	0	0	$(y'z', z'x')$

Table 5: Character Table for Group of Axis in

3rd Nearest Neighbour Direction

	x'y'z'	$\bar{x}$'y'z'	Types of d-function
Γ_1	1	1	$(3z'^2 - r^2)$;$(x'^2 - y'^2)$;y'z'
Γ_2	1	-1	x'y' ; z'x'

Table of Coefficients of $J_t^{(n'm')}$ in Formulae for $J_{tu}^{(nm)}$

Table 6: Nearest Neighbours

		$J_1^{(1'1')}$	$J_1^{(2'2')}$	$J_1^{(3'3')}$	$J_1^{(4'4')}$	$J_1^{(5'5')}$	$J_1^{(4'5')}$
$R_{1u} = a(\frac{1}{2},0,\frac{1}{2})$ and $a(0,\frac{1}{2},\frac{1}{2})$	$J_{1u}^{(11)}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	0
	$J_{1u}^{(44)}$	0	0	$\frac{1}{4}$	$\frac{9}{16}$	$\frac{3}{16}$	$\frac{3\sqrt{3}}{8}$
	$J_{1u}^{(55)}$	0	0	$\frac{3}{4}$	$\frac{3}{16}$	$\frac{1}{16}$	$\frac{\sqrt{3}}{8}$
	$J_{1u}^{(11)}$	0	0	0	$\frac{1}{4}$	$\frac{3}{4}$	$\frac{-\sqrt{3}}{2}$
$R_{1u} = a(\frac{1}{2},\frac{1}{2},0)$	$J_{1u}^{(44)}$	0	0	1	0	0	0
	$J_{1u}^{(55)}$	0	0	0	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{\sqrt{3}}{2}$

Table of Coefficients of $J_b^{(n'n')}$ in Formulae for $J_{ba}^{(nn)}$

Table 7: Next Nearest Neighbours

		$J_2^{(1'1')}$	$J_2^{(2'2')}$	$J_2^{(4'4')}$	$J_2^{(5'5')}$
$R_{2u} = a(1,0,0)$ and $a(0,1,0)$	$J_{2u}^{(11)}$	0	1	0	0
	$J_{2u}^{(44)}$	0	0	$\frac{1}{4}$	$\frac{3}{4}$
	$J_{2u}^{(55)}$	0	0	$\frac{3}{4}$	$\frac{1}{4}$
$R_{3u} = a(0,0,1)$	$J_{3u}^{(11)}$	1	0	0	0
	$J_{3u}^{(44)}$	0	0	1	0
	$J_{3u}^{(55)}$	0	0	0	1

Table of Coefficients of $J_{\xi}^{(n'm')}$ in Formulae

for $J^{(nm)}$

Table 8: 3rd Nearest Neighbours

	$J_3^{(1'1')}$	$J_3^{(2'2')}$	$J_3^{(3'3')}$	$J_3^{(4'4')}$	$J_3^{(5'5')}$	$J_3^{(4'5')}$	$J_3^{(1'3')}$	$J_3^{(2'4')}$	$J_3^{(2'5')}$
$J_{3u}^{(11)}$	$\frac{1}{6}$	$\frac{1}{18}$	$\frac{1}{5}$	$\frac{1}{9}$	$\frac{1}{3}$	$\frac{2\sqrt{5}}{9}$	$\frac{\sqrt{2}}{5}$	$-\frac{\sqrt{2}}{9}$	$-\frac{\sqrt{6}}{9}$
$R_{3u}=a(1,\frac{1}{2},\frac{1}{2})$ $J_{3u}^{(44)}$	$\frac{1}{6}$	$\frac{1}{2}$	$\frac{1}{12}$	$\frac{1}{16}$	$\frac{5}{16}$	$-\frac{\sqrt{5}}{8}$	$-\frac{\sqrt{2}}{6}$	$-\frac{\sqrt{2}}{4}$	$\frac{\sqrt{6}}{4}$
or $a(\frac{1}{2},1,\frac{1}{2})$ $J_{3u}^{(55)}$	$\frac{1}{2}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{48}$	$\frac{1}{16}$	$-\frac{\sqrt{5}}{24}$	$-\frac{\sqrt{2}}{2}$	$-\frac{\sqrt{2}}{12}$	$\frac{\sqrt{6}}{12}$
$J_{3u}^{(11)}$	0	$\frac{2}{9}$	0	$\frac{25}{36}$	$\frac{1}{12}$	$-\frac{5\sqrt{5}}{18}$	0	$\frac{5\sqrt{2}}{9}$	$-\frac{\sqrt{6}}{9}$
$R_{3u}=a(\frac{1}{2},\frac{1}{2}\ 1)$ $J_{3u}^{(44)}$	$\frac{2}{5}$	0	$\frac{1}{5}$	0	0	0	$-\frac{2\sqrt{2}}{5}$	0	0
$J_{3u}^{(55)}$	0	$\frac{2}{5}$	0	$\frac{1}{12}$	$\frac{1}{4}$	$-\frac{\sqrt{5}}{6}$	0	$-\frac{\sqrt{2}}{3}$	$\frac{\sqrt{6}}{3}$

Table 9: Two-centre Contributions to Energy Integrals (Rydbergs). The Quantities Tabulated are Defined by Equations (5.31) to (5.35)

	t = 1	t = 2	t = 3	t = 4
$I_t^{(1'1')} \times 10^2$	-0.704	-0.134	-0.0445	-0.0187
$I_t^{(2'2')} \times 10^2$	2.44	0.554	0.211	0.0995
$I_t^{(5'5')} \times 10^2$	-2.83	-0.747	-0.311	-0.161
$E_t^{(1'1')} \times 10^2$	2.60	1.25	0.610	0.325
$E_t^{(2'2')} \times 10^2$	-1.60	-2.00	-1.76	-1.24
$E_t^{(5'5')} \times 10^2$	0.495	0.665	0.923	1.03
$F_t^{(1'1')} \times 10^2$	-3.30	1.38	-0.654	-0.344
$F_t^{(2'2')} \times 10^2$	4.04	2.55	1.97	1.34
$F_t^{(5'5')} \times 10^2$	-3.33	-1.41	-1.23	-1.19

	t = 5	t = 6	t = 7	t = 8	t = 9
$F_t^{(1'1')} \times 10^3$	-1.74	-1.01	-0.597	-0.362	-0.224
$F_t^{(2'2')} \times 10^3$	8.81	5.47	3.68	2.48	1.68
$F_t^{(5'5')} \times 10^3$	-8.85	-7.49	-5.97	-4.61	-3.49

Table 10: Non-orthogonality Integrals

	t = 1	t = 2	t = 3	t = 4
$S_t^{(1'1')} \times 10^2$	5.69	2.28	1.05	0.534
$S_t^{(2'2')} \times 10^2$	-7.46	-4.67	-3.40	-2.21
$S_t^{(5'5')} \times 10^2$	4.09	2.73	2.41	2.19

	t = 5	t = 6	t = 7	t = 8	t = 9
$S_t^{(1'1')} \times 10^2$	0.271	0.155	0.0985	0.0537	0.0321
$S_t^{(2'2')} \times 10^2$	-1.33	-0.668	-0.568	-0.375	-0.249
$S_t^{(5'5')} \times 10^2$	1.62	1.39	0.985	0.736	0.543

Table 11: Three-centre Integral Contributions to Nearest Neighbour Energy Integrals

The first column gives the co-ordinates of a typical potential centre referred to axes Ox'y'z' of figure 10 and numbers in brackets on the left refer to centres marked in the figure. The second column gives the number of centres making the same contribution.

Centre	No. of equivalent centres	10^2 x contribution of one centre to $G_1^{(1'1')}$	$G_1^{(2'2')}$	$G_1^{(3'3')}$	$G_1^{(4'4')}$	$G_1^{(5'5')}$	$G_1^{(4'5')}$
(1)$a(\frac{a}{4},\frac{1}{2},\frac{a}{4})$	4	-1.59	1.96	1.02	-0.475	0.029	-0.052
(2)$a(\frac{a}{2},0,0)$	2	-0.049	0.002	0.095	-1.90	0.422	-0.143
$a(\frac{a}{2},0,\frac{a}{2})$	2	-0.048	0.002	0.095	-1.90	0.422	1.09
(3)$a(\frac{a}{4},\frac{1}{2},\frac{a}{4})$	4	-0.075	-0.279	-0.104	-0.030	0.065	0.154
$a(\frac{a}{4},\frac{1}{2},\frac{3a}{4})$	4	-0.075	-0.279	-0.104	-0.030	0.065	0.195
(4)$a(0,1,0)$	2	-0.006	0.008	0.000	-0.170	0.004	0.002
$a(0,1,\frac{a}{2})$	2	-0.006	0.006	0.000	-0.170	0.004	-0.137
$G_1^{(n'm')} \times 10^2$		-7.17	5.65	3.62	-10.4	2.33	2.02

Table 12: Three-centre Integral Contributions to

Next Nearest Neighbour Energy Integrals

The first column gives the co-ordinates of a typical potential centre referred to axes $Ox'y'z'$ of figure 11 and numbers in brackets on the left refer to centres marked in the figure. The second column gives the number of centres making the same contribution.

Centre	No. of equivalent centres	10^2 x contribution of one centre to $G_2^{(1'1')}$	$G_2^{(2'2')}$	$G_2^{(4'4')}$	$G_2^{(5'5')}$
(1) $a(0,\frac{1}{2},\frac{1}{2})$	2	-0.094	5.30	-0.682	-0.537
(2) $a(\frac{1}{2},0,\frac{1}{2})$	2	-0.094	0.14	-0.682	-0.537
(3) $a(\frac{1}{2},\frac{1}{2},0)$	8	-0.215	0.03	-0.014	0.224
$G_2^{(n'm')} \times 10^2$		-2.08	13.4	-2.84	-0.36

Table 13: Three-centre Integral Contributions to Third Nearest Neighbour Energy Integrals

The first column gives the co-ordinates of a typical potential centre referred to axes Ox'y'z' of figure 12 and numbers in brackets on the left refer to centres marked in the figure. The second column gives the number of centres making the same contribution.

Centre	No. of equivalent centres	10^2 x contribution of one centre to $G_3^{(1'1')}$	$G_3^{(2'2')}$	$G_3^{(3'3')}$	$G_3^{(4'4')}$	$G_3^{(5'5')}$	$G_3^{(4'5')}$	$G_3^{(2'5')}$	$G_3^{(2'4')}$	$G_3^{(1'3')}$
(1) $a(\frac{\sqrt{2}}{4}, 0, \frac{\sqrt{24}}{8})$	2	-0.093	0.178	2.26	-0.174	-2.13	-0.513	0	0	0
(2) $a(0, \frac{\sqrt{3}}{3}, \frac{\sqrt{6}}{6})$	1	-0.037	1.25	0.036	-0.269	-0.007	0.355	0.357	-0.386	-0.052
$a(0, \frac{\sqrt{3}}{3}, \frac{\sqrt{6}}{3})$	1	-0.037	1.25	0.036	-0.269	-0.007	0.015	-0.071	0.775	0.026
(3) $a(\frac{\sqrt{2}}{4}, \frac{\sqrt{3}}{3}, \frac{\sqrt{6}}{12})$	2	-0.109	0.322	0.101	-0.331	0.168	0.161	-0.240	0.040	0.205
$a(\frac{\sqrt{2}}{4}, -\frac{\sqrt{3}}{3}, \frac{5\sqrt{6}}{12})$	2	-0.109	0.322	0.101	-0.331	0.168	-0.031	-0.042	-0.170	-0.048
$G_3^{(n'm')} \times 10^2$		-0.68	4.14	4.99	-1.93	-4.21	-0.20	0.30	0.13	0.29

Table 14: Three-centre Integral Contributions to Fourth Nearest Neighbour Energy Integrals

The first column gives the co-ordinates of a typical potential centre referred to axes Ox'y'z' of figure 13 and numbers in brackets on the left refer to centres marked in the figure. The second column gives the number of centres making the same contribution.

	Centre	No. of equivalent centres	10^2 x contribution of one centre to $G_4^{(1'1')}$	$G_4^{(2'2')}$	$G_4^{(3'3')}$	$G_4^{(4'4')}$	$G_4^{(5'5')}$	$G_4^{(4'5')}$
(1)	$a(0,0,\frac{\sqrt{2}}{2})$	1	-0.004	0.189	0.189	-0.004	-3.95	0
(2)	$a(\frac{\sqrt{2}}{4},\frac{1}{2},\frac{\sqrt{2}}{4})$	4	-0.090	0.300	0.165	-0.019	0.022	0.010
	$a(\frac{\sqrt{2}}{4},\frac{1}{2},\frac{3\sqrt{2}}{4})$	4	-0.090	0.300	0.165	-0.019	0.022	-0.001
	$G_4^{(n'm')} \times 10^3$		-0.72	2.59	1.51	-0.15	-3.75	0.07

Table 15: Values of Energy Integrals $J_t^{(n'm')}$

	t = 1	t = 2	t = 3	t = 4
$J_t^{(1'1')} \times 10^2$	-10.5	-3.46	-1.33	-1.07
$J_t^{(2'2')} \times 10^2$	9.67	16.0	6.11	3.93
$J_t^{(3'3')} \times 10^2$	7.66	16.0	6.96	2.85
$J_t^{(4'4')} \times 10^2$	-15.7	-4.22	-2.61	-0.495
$J_t^{(5'5')} \times 10^2$	-0.983	-1.77	-5.44	-4.94
$J_t^{(4'5')} \times 10^2$	2.82	0	-0.198	0.035
$J_t^{(1'3')} \times 10^2$	0	0	0.290	0
$J_t^{(2'4')} \times 10^2$	0	0	0.130	0
$J_t^{(2'5')} \times 10^2$	0	0	0.299	0

	t = 5	t = 6	t = 7	t = 8	t = 9
$J_t^{(1'1')} \times 10^2$	-0.599	-0.341	-0.199	-0.199	-0.078
$J_t^{(2'2')} \times 10^2$	2.97	1.91	1.36	0.957	0.559
$J_t^{(5'5')} \times 10^2$	-3.43	-2.77	-2.14	-1.62	-1.20

PART 2.

THE ROLE OF THE D BAND IN FERROMAGNETISM

CHAPTER 6

THE THERMODYNAMIC PROPERTIES OF FERROMAGNETIC METALS

The theory of ferromagnetism in the transition metals is one of the most controversial subject in solid state physics. Much of the controversy has been over the question of whether the electrons responsible for ferromagnetism are bound on atoms or whether a band picture applies. At one time a considerable draw-back to the band theory was its apparent inability to deal with the existence of spin waves, which are observed directly and indirectly. Recent work, including some by the author on which this part of the thesis is based, has shown that spin waves do emerge from a band approach but only if one goes beyond the Hartree-Fock approximation. In the transition metals iron, cobalt and nickel it is the d electrons which are responsible for ferromagnetism. It therefore appears that the d band in these metals plays a dominant role in the whole phenomenon of ferromagnetism, even in the phenomenon of spin waves which has usually been associated with localized electrons.

This chapter deals qualitatively with the low-lying states of a ferromagnetic metal and the consequent low temperature thermodynamic properties. A simple picture of a spin wave is given. The situation

at higher temperatures, near and above the Curie point, is also briefly discussed as is the present status of collective electron theory. Chapter 7 gives a detailed treatment of the band theory of spin waves. It is first of all appropriate to give an account of previous work.

19. Introduction to ferromagnetism in metals

This discussion is restricted to the theory of the spontaneous magnetization as opposed to domain theory and the theory of the magnetization curve. To explain the spontaneous magnetization Weiss (1907) postulated the existence of a 'molecular field' which was proportional to the magnetization and acted on the individual magnetic carriers. It is now known from measurements of the gyromagnetic ratio that these carriers are electron spins. Weiss' theory, particularly when the original classical form is modified to allow for the discrete orientation of electron spin, gives reasonable qualitative agreement with the following experimental facts: (1) the observed decrease of the magnetization to zero at the Curie temperature θ, (2) the Curie-Weiss law for the temperature variation of susceptibility above the Curie temperature, (3) the magnetic specific heat. However a very large molecular field ($\sim 10^7$ gauss in magnetic terms)

is required to give the observed values of θ. The origin of the 'molecular field' remained a mystery until Heisenberg (1928) traced it to the effects of exchange interaction between electrons. Heisenberg's work was based on the Heitler-London model in which electrons are localized on atoms. Bloch (1929) subsequently considered the case of a free electron gas and showed that the Hartree-Fock approximation predicts ferromagnetism for all electron densities below a certain value which lies just below the metallic range. Wigner (1938) and Pines (1955) have since pointed out that in fact correlation effects make it very unlikely that the free electron gas is ferromagnetic in any density range. No doubt ferromagnetism can be produced if a sufficiently large effective mass is introduced.

Most subsequent work has stemmed from these early contributions of Heisenberg and Bloch, the one based on the Heitler-London model and the other on an itinerant model. The former approach will not be discussed in detail here since it is unable to deal with the fact that in nickel and cobalt the saturation magnetic moment corresponds to non-integral numbers of unpaired spins per lattice site. In iron this number is 2.2 and, allowing for some polarization of the S electrons, it is possible that a localized model with two magnetic electrons on each atom could apply (see Mott and Stevens 1957). The localized model certainly applies to the rare earth metals and to insulators such as ferrites and garnets. The result of the localized model which is of

most significance for the present discussion was obtained by Bloch (1932). He showed that the low-lying states of the Heitler-London-Heisenberg model consist of a number of almost independent spin wave excitations. In a spin wave a spin reversal propagates through the crystal from atom to atom with a wave-vector $\underline{K}$. The excitation energy of a spin wave is proportional to K^2, and by applying Bose-Einstein statistics it is found that both the deviation of the magnetization from saturation and the associated specific heat vary with temperature T as $T^{3/2}$, for $T \ll \theta$. These $T^{3/2}$ laws are observed experimentally and more direct evidence of the existence of spin waves in ferromagnetic metals and alloys is provided by inelastic neutron-scattering experiments (Lowde 1956, Sinclair and Brockhouse 1960) and spin-wave resonance work (Tannenwald 1961). A satisfactory theory of ferromagnetism must therefore lead to spin waves, but it has been pointed out that the localized model in which they appear so naturally is unsuitable from other points of view, at least for nickel and cobalt.

The first application of band theory to ferromagnetism was made by Slater (1936) for the case of nickel. It is pointed out in section 21 that his analysis is inaccurate although he obtained a reasonable estimate of the Curie temperature. The most systematic application of band theory to ferromagnetism is the 'collective electron' theory of

Stoner (1938, 1939). Stoner treats the holes in the d band as n particles in a parabolic band, although the assumption of a particular band shape is not an essential part of the theory and other band shapes have been considered (Wohlfarth 1951). Exchange interaction is introduced by assuming that the difference in energy of a particle in the same Bloch state with spin parallel and anti-parallel to the magnetization is $2k\theta'\gamma$. $k\theta'$ is a measure of the exchange interaction where k is Boltzmann's constant, and γ is the relative magnetization, i.e. the ratio of the magnetic moment of the system to that with all n spins alined. It is further assumed that Fermi-Dirac statistics may be applied to the particles with their one-electron energies modified in this way. Stoner's treatment is based implicitly on a model system whose energy states are given by a sum of one-electron energies and an interaction term $\frac{1}{4}nk\theta'\gamma^2$. Lidiard (1951, 1952) and Meyer (1957) have shown that if the normal methods of statistical mechanics are applied to such a system, the results are identical with those obtained by Stoner's simplified statistical method. A basis for Stoner's model was sought (Lidiard 1951, Wohlfarth 1953, Tredgold 1954) within the Hartree-Fock approximation but difficulties were immediately encountered. The exchange energy does not take the simple form $\frac{1}{4}nk\theta'\gamma^2$ because the individual exchange integrals between Bloch states depend very strongly on the difference in wave-vector between the states involved. Lidiard (1951) pointed out that Stoner's exchange energy is only

obtained if the exchange integral is a constant. He further pointed out that this would be the case if the effective interaction between particles were of sufficiently short range, although at that time no justification could be given for such an assumption. The use of a short range interaction now appears reasonable on the basis of Bohm and Pines' (1953) plasma theory and a discussion of of the present status of Stoner's collective electron theory is given in section 21. Collective electron theory correlates successfully data such as saturation magnetization, the Curie point, susceptibility above the Curie point, and low temperature electronic specific heat for a wide variety of metals and alloys, (see Wohlfarth 1953 and references given there, Wohlfarth 1956, [illegible] and Wohlfarth 1963). However no spin waves appear in the conventional form of the theory. The first band theory of spin waves was given by Slater (1937) but he considered only the case of a ferromagnetic insulator with one electron per atom. Slater showed that the energy spectrum of states with total spin $S' - 1$ and total wave-vector $\underline{K}$, where S' is the total spin in the ferromagnetic ground state, is as shown in figure 19. The lowest branch of the spectrum consists of exciton-like states which correspond to spin waves and the continuum corresponds to band-type excitations. The work of section 30 constitutes a generalization of Slater's work to the case of a metal.

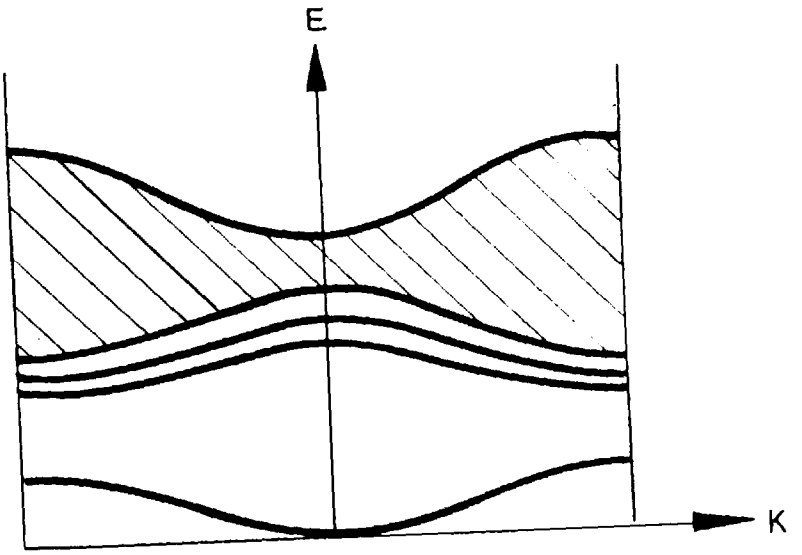

Fig. 19

Herring and Kittel (1951) made the first progress on the problem of spin waves in metals. Their treatment for cubic crystals is based on the macroscopic exchange energy

$$A\left[(\nabla\alpha_1)^2+(\nabla\alpha_2)^2+(\nabla\alpha_3)^2\right] \qquad (6.1)$$

which is of importance in the theory of the Bloch wall between domains. $\alpha_1, \alpha_2, \alpha_3$ are the cosines of the angles the magnetization vector makes with the cubic axes and A is the exchange stiffness constant for the material considered. Herring and Kittel's phenomenological approach is to set up a Hamiltonian involving spin density operators which is based on the energy (6.1). Spin waves of long wavelength are derived formally by treating the ferromagnetic material as a continuous medium in which

the components of the spin density operators are regarded as amplitudes of a vector field which is quantized in the way demanded by the known commutation relations for spin components. This quantized phenomenological approach, or its counterpart in which the Hamiltonian is treated classically, has proved very valuable in discussing the interactions with microwave fields which occur in ferromagnetic resonance and allied effects (see the review by Akhiezer, Bar' Yakhtar and Kaganov 1960). However, this approach only deals with the spin-wave part of the energy spectrum and throws no light on the relation between spin-wave theory and collective electron theory. This problem can only be solved by examining the eigenstates of the full Hamiltonian of the system. Herring and Kittel deal with the problem of obtaining spin-wave eigenstates in an indirect way by considering the response of the saturated specimen to a small perturbing magnetic field. If the unperturbed magnetization vector is in the z direction the perturbing field considered is applied in the y direction and varies sinusoidally in space in the x direction with a long wavelength $2\pi/K$. The magnetization responds to the perturbation and it is shown by a formal perturbation calculation that an energy of the form (6.1) only results if stationary states of the system, with small total wave-vector $\underline{K}$ and total spin $S' - 1$, exist with energies $O(K^2)$ above the ferromagnetic ground state. (It is assumed the latter state has zero total wave-

vector and total spin S' where spin is measured in units of $\hbar$.) These states are identified as spin waves and a method of obtaining their wave functions and energies is outlined. It is not clear within what approximation the states obtained are actually eigenfunctions of the system. Herring (1952b) was able to carry the method through in detail by making a further approximation.

Herring and Kittel suggest that the low-energy states of ferromagnetic metal are of two types: the band-type states of collective electron theory with 'no spin waves excited' and states derived from these by excitation of spin waves. It is further suggested that the contributions of collective electron and spin-wave excitations to the specific heat may be additive. These ideas are described as "very much in the realm of speculation" and it one of the aims of this chapter to make them more definite (see Edwards 1962). Other work with the same aim but using quite different methods is that of Vonsovsky and Kobelev (1961) and Ruijgrok (1962). Work by Izuyama (1960) on spin waves in the band model should be mentioned. He uses field theoretical methods and his approximation is equivalent to Herring's (1952b) as is shown in section 24.2 of this thesis.

The work described in this part of the thesis is restricted to a single-band model of a metal for simplicity. There is little doubt that the qualitative results of this chapter hold even in the case of several overlapping bands. Magnetic and spin-orbit interactions are neglected throughout the work.

20. The low-lying states of a ferromagnetic metal

Consider a model which consists of 2N-n electrons in a single band containing N-states of each spin, where n<<N, and assume that the ground state of the system is that of maximum multiplicity with total spin S' equal to $\frac{1}{2}n$. (Spin is measured throughout in units of $\hbar$). At first only the low-lying states of the system with S' equal to $\frac{1}{2}n$ or $\frac{1}{2}n-1$ will be discussed and it is sufficient to consider those states which have S' and the z component of spin S'_z equal. Suppose Ψ is the eigenfunction of such a state; then if S_x, S_y are x and y components of spin the functions

$$(S_x - iS_y)\Psi, \quad (S_x - iS_y)^2\Psi, \quad (S_x - iS_y)^{2S'}\Psi$$

represent states degenerate with Ψ and of the same total spin S' but with successively lower values of S'_z equal to

$$S' - 1, \quad S' - 2, \ldots\ldots\ldots\ldots -S'$$

Any eigenstate with $S'_z < S'$ may be derived in this way and it will emerge that the state $(S_x - iS_y)^l\Psi$ may be regarded as formed from Ψ by creating l spin waves of zero vector.

The whole discussion here is based on a band description of the metal, although correlation effects are considered. An eigenfunction of the system may be written as a linear combination of Slater determinants formed form one-electron functions $b(\underline{k}, r_1)\alpha(1)$ and $b(\underline{k}, r_1)\beta(1)$

where $\underline{r}_i$ is the position of the i^{th} electron, $b(\underline{k}, \underline{r}_i)$ is a Bloch function with wave vector $\underline{k}$ and $\alpha(i)$, $\beta(i)$ are the eigenfunctions of σ_{iz}, the z component of spin of the i^{th} electron, with eigenvalues $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively.

In a state with $S_z' = \frac{1}{2}n$ the α spin sub-band is full and the β spin sub-band contains n holes. The low-lying states with $S_z' = \frac{1}{2}n$ may be described as having a full α spin band and a partially full β spin band with a few electron-like quasi-particles just outside the Fermi surface and an equal number of hole-like quasi-particles just within it. These quasi-particles are essentially independent and any state which may be described as derived from the ground state by exciting a number of independent quasi-particles will be referred to as a 'band-type' state. Such a state has a direct correspondence with an eigenfunction of the system in which electronic interactions are neglected i.e. direct correspondence with a single Slater determinant. Band-type states are those normally considered in collective electron theory and correspond to the states with "no spin waves excited" discussed by Herring and Kittel (1951).

States with $S_z' = \frac{1}{2}n-1$, that is with one reversed spin, are of three distinct types: (a) states with total spin $\frac{1}{2}n$ which are derived from states with $S_z' = \frac{1}{2}n$ by applying the operator $S_x - iS_y$; (b) band-type states with total spin $\frac{1}{2}n-1$ in which the additional electron in the β spin band behaves as an additional quasi-particle outside the Fermi surface and moves independently of the hole-like particle left in the

α spin band; (c) states with total spin $\frac{1}{2}n-1$ in which an electron in the β spin band and the hole in the α spin band are bound together in an exciton-like state characteristic of a spin wave.

These different types of states will now be discussed in a qualitative way. A more exact discussion of states of type (c) is given in Chapter 7.

Consider first a state of type (b) which differs from the ground state in having an electron-like quasi-particle just outside the Fermi surface in the β spin band and a hole-like quasi-particle near the top of the α spin band. The energy of such a state is of the form

$$E_0 + E_\beta(\underline{k}') - E_\alpha(\underline{k}) \qquad (6.2)$$

where E is the ground state energy and $E_\beta(\underline{k}')$, $E_\alpha(\underline{k})$ are quasi-particle energies in β and α spin bands respectively. The quasi-particle energies are only defined in regions of $\underline{k}$-space where the quasi-particles are long-lived, that is near the top of the α spin and near the Fermi surface in the β spin band. If the ferromagnetic state is stable, $E_\beta(\underline{k}') > E_\alpha(\underline{k})$ as shown in figure 20.

To establish the connection with collective electron theory it it convenient to define new energies

$$\epsilon_\alpha(\underline{k}) = E_\alpha(\underline{k}) + \tfrac{1}{2}J, \quad \epsilon_\beta(\underline{k}') = E_\beta(\underline{k}') - \tfrac{1}{2}J$$

where J is chosen so that $\epsilon_\alpha(k)$ and $\epsilon_\beta(k')$ become parts of a fairly smooth $\epsilon(k)$ curve as shown in figure 20. The energy (6.3) then becomes

$$E_0 + \epsilon(k') - \epsilon(k) + J \quad . \tag{6.3}$$

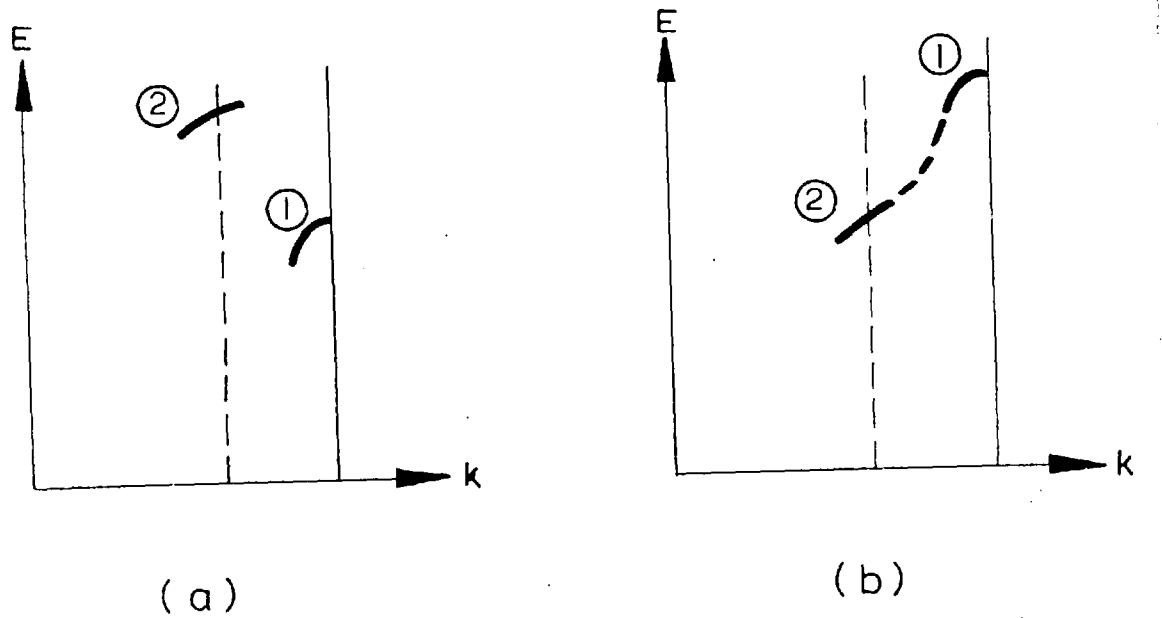

Fig.20(a) Curve 1 shows $\epsilon_\alpha(k)$ at the top of the band; curve 2 shows $E_\beta(k')$ at the Fermi surface.

Fig.20(b) Curves 1 and 2 show the redefined quasi-particle energies $\epsilon_\alpha(k)$ and $\epsilon_\beta(k')$.

For a general low-lying band-type state, with a number of hole-like quasi-particles in the α spin band and a number of quasi-particles excited in the β spin band, the energy may be written

$$E_0 - \sum_i p_{i\alpha}\left[\epsilon(k_i) - \tfrac{1}{2}J\right] + \sum_{i>f} n_{i\beta}\left[\epsilon(k_i) + \tfrac{1}{2}J\right] - \sum_{j<f} p_{j\beta}\left[\epsilon(k_j) + \tfrac{1}{2}J\right] \quad . \tag{6.4}$$

$p_{i\alpha}$ and $p_{j\beta}$ are occupation numbers for hole-like states and $n_{i\beta}$ is the occupation number for an electron-like quasi-particle state $\underline{k}_i$. The summations $i > f$, $j < f$ are to be carried out over states respectively outside and inside the Fermi surface in the β spin band. Expression (6.4) gives the energy of a typical state considered in collective electron theory where the parameter $k\theta'$ occurring in that theory is equal to $\frac{1}{2}J$. In the present formulation J is somewhat arbitrary but the band form $\epsilon(\underline{k})$ also depends on J. In fact (6.4) really involves only the quasi-particle energies $E_\beta(\underline{k}')$, $E_\alpha(\underline{k})$ which are the physically significant quantities. The constant 'exchange energy' J has been introduced merely to show that the energies of the low-lying band-type states of the system may be written in the form of (6.4) which corresponds to the low-lying states of collective electron theory. ~~It must be emphasized that the above arguments apply only to the low-lying states of the system.~~ It must be emphasized that the above very general arguments apply only to the low-lying states of the system. More restrictive conditions must be assumed or proved to justify collective electron theory at higher temperatures. This is considered in section 21.

20.1 Spin-wave states

A discussion of states of type (c) will now be given using an approximation equivalent to that made by Herring (1952b). A more exact discussion of states of type (c) is given in Chapter 7.

A state with $S_z' = \frac{1}{2}n$ may be represented approximately by a Slater determinant of total wave-vector $\underline{f}$

$$\Psi_\lambda^{(f)} = [(2N-n)!]^{-\frac{1}{2}} \Delta \{ \underline{k}_{1\alpha} \cdots \underline{k}_{N\alpha} ; \underline{k}_{1\beta} \cdots \underline{k}_{N-n,\beta} \} \tag{6.5}$$

which contains the one-electron functions $b(\underline{k}_{i\alpha}, \underline{r}_j)\alpha(j)$ and $b(\underline{k}_{i\beta}, \underline{r}_j)\beta(j)$. If a Wannier function $a(\underline{r}-\underline{R})$ is defined by

$$a(\underline{r} - \underline{R}) = N^{-\frac{1}{2}} \sum_{\underline{k}} \exp(-i\underline{k}_l \cdot \underline{R}) b(\underline{k}_l, \underline{r}), \tag{6.6}$$

where the summation is over all wave-vectors $\underline{k}_l$, (6.5) may be written as

$$\Psi_\lambda^{(f)} = [(2N-n)!]^{-\frac{1}{2}} \Delta \{ \underline{R}_{1\alpha}, \cdots \underline{R}_{N\alpha} ; \underline{k}_{1\beta} \cdots \underline{k}_{N-n,\beta} \} \tag{6.7}$$

which is a determinant containing functions $a(\underline{r}_j - \underline{R}_l)\alpha(j)$ and $b(\underline{k}_{l\beta}, \underline{r}_j)\beta(j)$. Approximate wave functions for states with $S' = \frac{1}{2}n-1$ and total wave-vector $\underline{f} + \underline{K}$ may be formed as linear combinations of $\theta_\lambda^{(f)}(\underline{k} - \underline{K}, \underline{k})$ determinants obtained from (6.5) by replacing $b(\underline{k} - \underline{K}, \underline{r}_j)\alpha(j)$ by $b(\underline{k}, \underline{r}_j)\beta(j)$ where the latter state is unoccupied in (6.5). It follows from Herring's work (Herring 1952b) and from Section 24.1 of this thesis that within this approximation stationary states exist with wave functions of the form

$$n^{-\frac{1}{2}} \sum_{\underline{k}}^{(\bar{\lambda})} \theta_\lambda^{(f)}(\underline{k}_t - \underline{K}, \underline{k}_t) + o(K) \tag{6.8}$$

for small K where $\sum^{(\bar{\lambda})}$ denotes summation over $\underline{k}$-vectors of states unoccupied in (6.5). The states (6.8) with $K \neq 0$ approximate to states of total spin $\frac{1}{2}n-1$ and in fact to states of type (c); their spin-wave character is easily seen in (6.8) is rewritten as

$$N^{-\frac{1}{2}} \sum_{s} \exp(i \underline{K} \cdot \underline{R}_s) \Delta_s \qquad (6.9)$$

where Δ_s is the determinant obtained from (6.7) by replacing the function $a(\underline{r}_j - \underline{R}_n)\alpha(j)$ by $a(\underline{r}_j - \underline{R})\beta(j)$, $a(\underline{r})$ being a localised function defined by

$$a(\underline{r}) = n^{-\frac{1}{2}} \sum_{t}^{(\bar{\lambda})} b(\underline{k}_t, \underline{r}) + O(K) \qquad (6.10)$$

A proof of the equivalence of (6.8) and (6.9) is given below. (6.9) is clearly a generalization of a Bloch spin wave.

It is straightforward to show that Δ_s, as defined above may be written

$$\Delta_s = n^{-\frac{1}{2}} \sum_{t}^{(\bar{\lambda})} [1 + O(K)] e^{-i \underline{k}_t \cdot \underline{R}_s} (-1)^{N-s}$$
$$\mathcal{A}\{a(\underline{r}_1 - \underline{R}_1)\alpha(1) \ldots a(\underline{r}_{s-1} - \underline{R}_{s-1})\alpha(s-1)$$
$$a(\underline{r}_s - \underline{R}_{s+1})\alpha(s) \ldots a(\underline{r}_{N-1} - \underline{R}_N)\alpha(N-1) b(\underline{k}_t, \underline{r}_N)\beta(N)$$
$$b(\underline{k}_1, \underline{r}_{N+1})\beta(N+1) \ldots b(\underline{k}_{N-n}, \underline{r}_{2N-n})\beta(2N-n)\} \qquad (6.11)$$

where $\mathcal{A}$ is a normalized antisymmetrizing operator acting on the electron coordinates. One may write $\mathcal{A}$ as

$$\mathcal{A} \equiv A\,\mathcal{A}_\alpha\,\mathcal{A}_\beta \tag{6.12}$$

where $\mathcal{A}_\alpha, \mathcal{A}_\beta$ are antisymmetrizing operators acting on electron coordinates in states of α and β spin respectively and A is an operator which sums over permutations of electron coordinates between the two spin sub-groups without regard to the ordering within each sub-group.

Using (6.11) and (6.12) one finds that expression (6.9) becomes

$$(Nn)^{-\frac{1}{2}} A \sum_s \sum_t^{(\bar{\lambda})} [1+o(K)] \exp[i(\underline{K}-\underline{k}_t)\cdot\underline{R}_s](-1)^{N-s}$$
$$\mathcal{A}_\alpha \{a(\underline{r}_1-\underline{R}_1)\alpha(1)\ldots a(\underline{r}_{s-1}-\underline{R}_{s-1})\alpha(s-1)\, a(\underline{r}_s-\underline{R}_{s+1})\alpha(s)$$
$$\ldots a(\underline{r}_{N-1}-\underline{R}_N)\alpha(N-1)\}$$
$$\mathcal{A}_\beta \{b(\underline{k}_t,\underline{r}_N)\beta(N), b(\underline{k}_1,\underline{r}_{N+1})\beta(N+1) \tag{6.13}$$
$$\ldots b(\underline{k}_{N-n},\underline{r}_{2N-n})\beta(2N-n)\}.$$

To simplify (6.13) consider the expression

$$\mathcal{A}\{b(\underline{k}_1,\underline{r}_1)\ldots b(\underline{k}_{q-1},\underline{r}_{q-1})b(\underline{k}_{q+1},\underline{r}_q)\ldots b(\underline{k}_N,\underline{r}_{N-1})\} \tag{6.14}$$

which is easily shown equal to

$$N^{-(N-1)/2} \sum_\lambda M_{q\lambda}\,\mathcal{A}\{a(\underline{r}-\underline{R}_\lambda)\ldots a(\underline{r}_{\lambda-1}-\underline{R}_{\lambda-1})a(\underline{r}_\lambda-\underline{R}_{\lambda+1})$$
$$\ldots a(\underline{r}_{N-1}-\underline{R}_N)\}$$

where M_{qi} is a minor of the complete N x N determinant

$$\delta = \| e^{i \underline{k}_r \cdot \underline{R}_s} \| .$$

Now

$$\delta = N^{N/2} e^{i\alpha} = N (-1)^{i+q} \exp(i \underline{k}_q \cdot \underline{R}_i) M_{qi}$$

where α is real and expression (6.14) therefore equals

$$e^{i\alpha} N^{-\frac{1}{2}} \sum_i (-1)^{i+q} \exp(-i \underline{k}_q \cdot \underline{R}_i) \, \mathrm{Pf} \{ a(\underline{r}_1 - \underline{R}_1) \ldots a(\underline{r}_{i-1} - \underline{R}_{i-1}) \, a(\underline{r}_i - \underline{R}_{i+1}) \ldots a(\underline{r}_{N-1} - \underline{R}_N) \} . \tag{6.15}$$

Using the equivalence of (6.14) and (6.15) and putting $\underline{k}_t - K = \underline{k}_q$ one may write (6.15), and therefore (6.9) as

$$e^{i\alpha} n^{-\frac{1}{2}} A \sum_t^{(\lambda)} [1 + o(1)] (-1)^{N+q} \mathrm{Pf}_\alpha \{ \phi(\underline{k}_1, \underline{r}_1) \alpha(1) \ldots \phi(\underline{k}_{q-1}, \underline{r}_{q-1}) \alpha(q-1) \, \phi(\underline{k}_{q+1}, \underline{r}_q) \alpha(q) \ldots \phi(\underline{k}_N, \underline{r}_{N-1}) \alpha(N-1) \}$$
$$\mathrm{Pf}_\beta \{ \phi(\underline{k}_t, \underline{r}_N) \beta(N) , \phi(\underline{k}_1, \underline{r}_{N+1}) \beta(N+1) \ldots \phi(\underline{k}_{N-n}, \underline{r}_{2N-n}) \beta(2N-n) \}$$
$$= e^{i\alpha} n^{-\frac{1}{2}} \sum_t^{(\lambda)} [1 + o(1)] \, \theta_\lambda^{(q)} (\underline{k}_t - \underline{K}, \underline{k}_t) .$$

Thus apart from a possible phase factor (6.8) and (6.9) are entirely equivalent.

A spin wave in a single-band model of a metal may thus be pictured as follows. Consider first a state of maximum spin alinement in which the β spin electrons partially fill a band of Bloch functions, and the α spin electrons may be described either as completely filling such a band or as filling a set of Wannier functions, one on each atom. The determinant Δ_s appearing in (6.9) is now obtained by removing an α spin electron from the Wannier function at the s^{th} lattice site, reversing its spin and placing it in a "partial" Wannier function $a(\underline{r} - \underline{R}_s)$ localized about the same lattice site. This partial Wannier function is formed only from otherwise unoccupied Bloch functions and is less localized than the Wannier functions $a(\underline{r} - \underline{R}_s)$. The wave function (6.9) thus represents a situation in which the β spin electron and α spin hole move together through the crystal like an exciton with wave-vector $\underline{K}$. The energy of this spin wave state is of the form $E_\lambda + CK^2 + O(K^3)$ for a given direction of $\underline{K}$ where E_λ is the energy of the state $\psi_\lambda^{(\beta)}$ from which the spin-wave state was derived. C is a constant which, for cubic crystals, is independent of the direction of $\underline{K}$ and which is effectively the same for all low-lying initial states $\psi_\lambda^{(\beta)}$; C must be positive, of course, for the ferromagnetic state to be stable. It is clear from (6.4) that the wave functions of spin-wave states contain almost equal contri-

butions from many Slater determinants and this property persists in the more exact description of these states given in Chapter 7. Thus a spin wave state does not have a correspondence with a single determinantal function of the interaction-free system and is, therefore quite distinct from a band-type state.

The limitation of the above discussion to spin-wave states derived from states with $S_z' = \frac{1}{2}n$ is not a real one and in fact spin wave states may be derived from any low-lying band-type state. Consider a low-lying band state with $S' = S_z' = \frac{1}{2}n-m$. This state may be pictured as differing from the ground state by having m occupied Bloch states just outside the Fermi surface in the β spin band and m unoccupied Bloch states at the top of the α spin band. The wave function of such a state may be represented approximately by the appropriate Slater determinant Ψ_λ. A state derived from this band-type state by exciting a spin wave of wave-vector $\underline{K}$ has the approximate wave function

$$(n-2m)^{-\frac{1}{2}} \sum_t \theta_\lambda(\underline{k}_t - \underline{K}, \underline{k}_t) + o(K), \tag{6.16}$$

where the summation is over the wave-vectors of Bloch states singly occupied in Ψ_λ and an approximate energy of the form $E_\lambda + CK^2$ for small K.

For the purpose of summing over states to treat the statistical

mechanics of the system it is necessary to enquire whether spin-wave states derived from different band-type states are necessarily independent. For example, it might be thought that the state of total wave-vector $\underline{p} + \underline{K}$ derived from $\psi_\lambda^{(\underline{p})}$ by exciting a spin wave $\underline{K}$ could be identical with the state derived from some other band-type state $\psi_\lambda^{(\underline{q})}$ by exciting a spin wave $\underline{p} - \underline{q} + \underline{K}$. In fact this is not the case as is shown by the following argument.

All low-lying band-type states must have a large number of singly occupied Bloch states in common and differ among themselves mainly through the occupation of states near the top of the α spin band and just outside the Fermi surface in the β spin band. It follows that a spin wave state (6.16) derived from a particular band-type state contains many determinants $\theta_\lambda(\underline{k}_t - \underline{K}, \underline{k}_t)$ which do not contribute to spin-wave states derived from any other band-type states. Thus all spin-wave states derived from different band-type states are independent and there is no fear of counting states twice through considering all spin wave excitations from all low-lying band-type states.

It remains to mention states of type (a). When $K = 0$ the states (6.8) reduce to $(S_x - iS_y)\psi_\lambda^{(\underline{p})}$ apart from a normalizing factor, and are thus states of type (a). States of type (a) are therefore states having a spin wave of zero wave-vector excited.

21. Statistical mechanics of the system

So far only states with one spin wave excited have been considered and to discuss the thermodynamics of the system a generalization must be made to the case of several spin wave excitations. In the case of an insulator it is known (Holstein and Primakoff 1940) that when a small number of spin wave states are excited the excitation energies are additive. It is reasonable to assume that this result holds in the present case for a state derived from a band-type state by exciting a small number of spin waves. Using the notation of expression (6.4) the energy of such a state may then be written in the form

$$E(\rho_{i\alpha}; n_{i\rho}; \rho_{j\beta}; N_\lambda) = E_c(\rho_{i\alpha}; n_{i\rho}; \rho_{j\beta}) + E_s(N_\lambda) \tag{6.17}$$

where E_c is the energy (6.4) of the band-type state and E_s is the total spin-wave excitation energy given by

$$E_s(N_1) = C \sum_\lambda N_1 K_1^2 \tag{6.18}$$

where N_1 is the occupation number for a spin-wave of wave-vector $\underline{K}_1$.

The partition function for the system in a magnetic field H in the z direction is

$$Z = Z_c Z_s \exp(\beta Hn/kT) \tag{6.19}$$

where

$$Z_c = \sum \exp\left[-\frac{E_c(\rho_{i\alpha}; n_{i\rho}; \rho_{j\rho}) + 2\beta H \sum_i \beta_{i\alpha}}{kT}\right] \tag{6.20}$$

and

$$Z_s = \sum_{N_1, N_2 \ldots} \exp\left[-\frac{E_s(N_i) + 2\beta H \sum N_i}{kT}\right] \tag{6.21}$$

In (6.20) the summation is over occupation numbers corresponding to all band-type states; β is the Bohr magneton.

The magnetization is then given by

$$M = \frac{kT}{V}\frac{\partial}{\partial H}\log Z = \frac{n\beta}{V} + \frac{kT}{V}\frac{\partial}{\partial H}\log Z_c + \frac{kT}{V}\frac{\partial}{\partial H}\log Z_s$$

$$= M_0 + M_c + M_s \tag{6.22}$$

where V is the volume of the crystal, M_0 is the saturation magnetization $n\beta/V$ and M_c, M_s are the deviations from saturation due to band-type and spin wave excitations respectively. When $H = 0$ the collective electron contribution is given by

$$M_c = -2\beta \exp(-\epsilon_g/kT) \int n(\epsilon) \exp[(\epsilon - \epsilon_m)/kT]\, d\epsilon \tag{6.23}$$

where ϵ_m is the maximum energy in the band $\epsilon(k)$ (using the

notation of section 20), $n(\epsilon)$ is the density of states in that band and ϵ_g is the minimum excitation energy when a spin is reversed. Thus

$$\epsilon_g = \epsilon_f - \epsilon_m + J$$

where ϵ_f is the energy at the Fermi surface in the β spin sub-band For a band with

$$n(\epsilon) = A(\epsilon_m - \epsilon)^p$$

(6.23) becomes

$$M_c = -2\beta A\,\Gamma(p+1)(kT)^{p+1}\exp(-\epsilon_g/kT) \qquad (6.24)$$

and this is equivalent to the usual collective electron theory expression when $p = \frac{1}{2}$. If at absolute zero neither spin sub-band is completely full M_0 no longer has the form (6.23) but is proportional to $-T^2$.

If spin-wave excitation energies are written in the form $J_s l^2 K^2$ where l is the side of the elementary cubic cell in the lattice (assumed cubic),

$$M_s = -0.0587\,\alpha\left(\frac{kT}{J_s}\right)^{\frac{3}{2}}\frac{M_0}{S} \qquad (6.25)$$

where α is $\frac{1}{2}$ for the body-centred lattice and $\frac{1}{4}$ for the face-centred and $\overline{S}$ is the mean spin (in units of $\hbar$) per lattice site at T = 0.

The specific heat at constant volume C_v is also given by the sum of two terms, one typical of collective electron theory and one of spin wave theory. Thus for H = 0

$$C_v = \frac{2}{3}\pi^2 k^2 T\, n(\epsilon_f) + 0.113\, N\alpha k \left(\frac{kT}{J_s}\right)^{3/2} \qquad (6.26)$$

where α has the same meaning as in (6.25). If at absolute zero neither spin sub-band is completely full the coefficient of T in the first term must be modified.

The qualitative arguments of this section cannot be regarded as rigorous, but it is believed they are essentially correct. They have been given in some detail since the problems considered have hardly been discussed in the literature since the work of Herring and Kittel nearly ten years ago. It is hoped that the present work may pave the way for more complete discussions. The main conclusions of the work, which support Herring and Kittel's original surmise, are that the low temperature specific heat of a ferromagnetic metal may be expressed as the sum of two terms, one of which may be calculated by collective electron theory and the other by normal spin-wave theory. A similar conclusion is reached concerning the deviation of the magnetization from saturation at low temperatures. Wohlfarth and Cornwell (1960) have attempted to analyse the data of Foner and Thompson (1959) on the

temperature variation of the magnetization of nickel by combining terms of the collective electron and spin-wave types. However they introduce weighting factors a and 1-a into the terms M_c and M_s, respectively, of (6.23) and this does not seem to be justified. A more correct analysis is being made by Wohlfarth and Thompson. Pugh and Argyle (1963) discuss their careful measurements on the temperature variation of the magnetization of nickel in terms of an expression of the type (6.23). However they use a T^2 term for M_c whereas as the exponential term (6.24) is probably more appropriate for nickel. On this basis they find that their results are best described by spin wave theory alone, but the presence of an exponential term would not appear to be excluded.

It must be emphasized again that the results obtained so far are restricted to low temperatures. At low temperatures, terms typical of collective electron theory must appear as long as some of the low-lying excitations may be described in terms of independent quasi-particles. The states of the system which are important at temperatures approaching the Curie point are very difficult to describe at all quantitatively and it is worth trying to formulate a qualitative picture of them. In a typical state there are a number of spin-wave excitations and a number of band-type excitations, and these must all interact to some extent. In the exciton-like picture of a spin wave described in section 30.1, the localization of the β spin electron about the α spin hole depends

on the number of unoccupied states in the β spin sub-band. In a state in which there are a considerable number of reversed spins the β spin electron will not be very localised about the corresponding α spin hole and spin-wave excitations will overlap each other. Above a certain density of spin wave excitations a pure band-type description of the state, albeit with strong correlation, may be correct. This idea is closely connected with Mott's (1961) ideas on the transition to the metallic state. Certainly well above the Curie point a band-type description should be appropriate. A band description is also appropriate at $0^{\circ}K$ and recent work by Rhodes and Wohlfarth (1963) is based on the assumption that conventional collective electron theory holds in these two regions of temperature. They emphasize that in the band scheme all the carriers need not have their spins alined at $0^{\circ}K$ i.e. the relative magnetization γ_o at $0^{\circ}K$ can be less than 1. γ_o can be deduced from the observed saturation magnetization and the Curie-Weiss constant, which yields the total number of carriers. It is found that for a wide range of metals and alloys, γ_o can be satisfactorily correlated with the Curie temperature θ, both of these quantities depending on the molecular field constant θ'. For substances with a low Curie point a very marked distinction is found between those which follow the band model, when γ_o is much less than 1, and those which follow a localised model where γ_o is always 1.

Unfortunately in the case of iron, with its high Curie point, it is not possible to make a decision between the two models.

The practical success of collective electron theory makes it very desirable to give a fundamental justification for the simple form of band-type state energies assumed by Stoner. It has been seen that spin waves are adequately dealt with on the band picture but that the situation at $0^{\circ}K$ and near to, and above the Curie point should be describable just in terms of band-type states. Liddiard (1951) showed that Stoner's theory of these states can be justified within the Hartree-Fock approximation if the effective interaction between carriers is of sufficiently short range. It was pointed out in section 3 that in the case of d bands the long-range part of the coulomb interaction cannot really be separated out by plasma theory. The situation from the viewpoint of plasma theory is further complicated by the fact that the cut-off wave-vector k_0 should surely depend on the state of magnetization. Nevertheless the interaction between carriers must certainly be screened since the d electrons are very polarizable. If one does assume a short-range interaction, collective electron theory can be justified qualitatively within the Hartree-Fock approximation. However, as stressed by Hubbard (private communication), the θ' thus calculated is an order of magnitude too large. This is because, with short-range correlation neglected, the chief contribution to θ' is the large coulomb energy ($\sim$ 10 e.v.) of two carriers on the same atom (see

Wohlfarth 1953). Wohlfarth (1953) and Van Vleck (1953) have suggested that short-range correlation is so important that two carriers hardly ever come together on the same atom. Such strong short-range correlation is perhaps surprising. However any other view appears to rule out the possibility of $J_o < 1$ and it is also difficult to understand why palladium is not then ferromagnetic. A calculation of the short-range correlation effect by the author is in progress. Slater (1936) effectively set out to calculate θ' for nickel with a Hartree-Fock approximation and considering mainly interaction effects on the same atom. The reason why he obtained an answer that was not much too large has been explained by Anderson (1961) in a footnote. Slater estimated the relevant integrals from spectroscopic data and apparently the large coulomb repulsion integral was allowed to drop out.

CHAPTER 7

THE BAND THEORY OF SPIN WAVES

A qualitative picture of spin waves in metals was given in section 20.1. In this chapter spin wave states are considered in more detail. A formal proof of the existence of spin waves in metals is given in section 22 and the accurate calculation of their energies is considered in section 23. The results of Herring (1952b) and Izuyama (1960) are obtained directly as special cases in section 24.

22. Proof of the Existence of spin waves

The work of Herring and Kittel on the existence of spin waves in metals was summarized in section 19. It was pointed out that their discussions depend on the assumption of a macroscopic exchange energy, and in the case of Herring (1952b) on an approximation such as has been used in Section 20. Since doubts have been expressed (Van Kranendonk and Van Vleck 1958) as to the existence in metals of spin waves with a well-defined wavelength, a more rigorous proof that such states exist seems desirable and it is the object of this section to supply this. It should be mentioned again that very direct experimental proof of the existence of spin waves in ferromagnetic metals and alloys is provided by the inelastic neutron scattering experiments of Lowde (1956)

and Sinclair and Brockhouse (1960), and by recent spin wave resonance work (Tannenwald 1961).

Consider a model of n electrons in a band containing N states of each spin, where $n < N$. Thus in the state of maximum spin alinement in the z direction there are n electrons in the α spin band and the β spin band is empty. This model is more convenient to deal with than that of Section 20 and the results may be applied to the previous model by interchanging the roles of electrons and holes. The Hamiltonian for the system is

$$H = \sum_i H_i + \tfrac{1}{2} \sum_{i \neq j} \sum v_{ij} + \text{constant}, \qquad (7.1)$$

where H_i is the sum of the kinetic energy of the i^{th} electron and its potential energy in the field of the ions and $v_{ij} = e^2/|r_i - r_j|$, the coulomb interaction between the i^{th} and j^{th} electrons. One-electron wave functions $b(\underline{k}, \underline{r})$ and energies $w(\underline{k})$ are defined by the equations

$$H\, b(\underline{k}, \underline{r}_i) = w(\underline{k})\, b(\underline{k}, \underline{r}_i). \qquad (7.2)$$

Suppose the ferromagnetic ground state of the system is non-degenerate with energy $\mathcal{E}$ and has zero total wave-vector. It is required to show that spin wave states with one reversed spin and wave-vector $\underline{K}$ exist with energies of the form

$$\mathcal{E} + CK^2 + O(K^3). \qquad (7.3)$$

At one point in the proof it seems necessary to assume that the crystal has a centre of inversion although one might have expected that the use of time-reversal symmetry would be sufficient.

Suppose the ground state wave function Ψ, corresponding to $S_z' = \frac{1}{2}n$ given by

$$\Psi = \sum_\lambda a_\lambda \Psi_\lambda \tag{7.4}$$

where the functions Ψ_λ are determinants formed from the one-electron wave functions $b(\underline{k}, \underline{r}_i) \propto (i)$. Thus one may write

$$\Psi_\lambda = \Delta(\underline{k}_1, \ldots \underline{k}_n)$$

and

$$\sum_t^{(\lambda)} \underline{k}_t = \underline{L} \tag{7.5}$$

where the summation is over the wave-vectors appearing in Ψ_λ and $\underline{L}$ is a reciprocal lattice vector. The set $\{\Psi_\lambda\}$ consists of all determinants satisfying (7.5) and in the present single-band model the functions of the set must differ from each other by changes of at least two one-electron functions. The ground state energy is

$$\mathcal{E} = \sum_\lambda |a_\lambda|^2 E_\lambda + \sum_{\lambda \neq \mu} \sum a_\lambda^* a_\mu \langle \Psi_\lambda | H | \Psi_\mu \rangle \tag{7.6}$$

where

$$E_\lambda = \langle \psi_\lambda | H | \psi_\lambda \rangle . \tag{7.7}$$

The second summation in (7.6) is over **all** pairs λ, μ such that ψ_λ and ψ_μ differ by two one-electron functions. Thus suppose

$$\psi_\lambda = \Delta (\underline{k}_1, \ldots \underline{k}_\ell, \ldots \underline{k}_m, \ldots \underline{k}_n) \tag{7.8}$$

and

$$\psi_\mu = \Delta (\underline{k}_1, \ldots \underline{k}_{\ell'}, \ldots \underline{k}_{m'}, \ldots \underline{k}_n), \tag{7.9}$$

then

$$\mathcal{E} = \sum_\lambda |q_\lambda|^2 E_\lambda + \sum_{\lambda \neq \mu} \sum q_\lambda^* q_\mu \left[\langle \ell m | v | \ell' m' \rangle - \langle \ell m | v | m' \ell' \rangle \right] \tag{7.10}$$

where

$$\langle \ell m | v | \ell' m' \rangle = \int \phi^* (\underline{k}_\ell, \underline{r}_1) \phi^* (\underline{k}_m, \underline{r}_2) v_{12} \phi (\underline{k}_{\ell'}, \underline{r}_1) \phi (\underline{k}_{m'}, \underline{r}_2) d\tau_{12} .$$

Throughout this section the suffixes l, m, l', m' are used in conjunction with λ , μ to denote the wave-vectors of the one-electron functions by which ψ_λ and ψ_μ differ. Another easily obtainable relation is

$$a_\mu^* \varepsilon = a_\mu^* E_\mu + \sum_{\lambda \neq \mu} a_\lambda^* [\langle lm|v|l'm'\rangle - \langle lm|v|m'l'\rangle]. \tag{7.11}$$

By analogy with equation (6.8) it might be expected that a state derived from Ψ by exciting a spin wave $\underline{K}$ would be approximately represented by the normalized λ wave function

$$\textcircled{H}_{\underline{K}} = \sum_\lambda a_\lambda \phi_{\lambda \underline{K}} \tag{7.12}$$

where

$$\phi_{\lambda \underline{K}} = n^{-\frac{1}{2}} \sum_s^{(\lambda)} \theta_\lambda(\underline{k}_s, \underline{k}_s + \underline{K}). \tag{7.13}$$

Here $\theta_\lambda(\underline{k}_s, \underline{k}_s + \underline{K})$ is the determinant derived from ψ_λ by replacing the Bloch function $b(\underline{k}_s, \underline{r}_i)\alpha(i)$ by $b(\underline{k}_s + \underline{K}, \underline{r}_i)\beta(i)$. Certainly $\textcircled{H}_0 \propto (S_x - iS_y)\Psi$ and is thus an exact eigenfunction corresponding to a state with a spin wave of zero wave-vector excited. $\textcircled{H}_{\underline{K}}$ will therefore be taken as a trial function and the energy associated with it

evaluated. Now

$$\begin{aligned}\langle \Theta_{\underline{S}} | H | \Theta_{\underline{K}} \rangle &= \varepsilon + \sum_{\lambda} |a_\lambda|^2 \left[\langle \phi_{\lambda \underline{K}} | H | \phi_{\lambda \underline{K}} \rangle - E_\lambda \right] \\ &\quad + \sum_{\lambda \neq \mu} \sum a_\lambda^* a_\mu \left[\langle \phi_{\lambda \underline{K}} | H | \phi_{\mu \underline{K}} \rangle - \langle \psi_\lambda | H | \psi_\mu \rangle \right]\end{aligned} \tag{7.14}$$

where the second summation is over all pairs λ, μ such that ψ_λ and ψ_μ differ by two one-electron functions. It is straightforward to show that

$$\begin{aligned}\langle \phi_{\lambda \underline{K}} | H | \phi_{\lambda \underline{K}} \rangle - E_\lambda &= n^{-1} \sum_t^{(\lambda)} \left[w_r (\underline{k}_t + \underline{K}) - w_r (\underline{k}_t) \right] \\ &\quad + n^{-1} \sum_s^{(\lambda)} \sum_t^{(\lambda)} \left[\langle s \underline{K}, t | v | s \underline{K}, t \rangle - \langle st | v | st \rangle \right. \\ &\qquad \left. - \langle t \underline{K}, s | v | s \underline{K}, t \rangle + \langle ts | v | st \rangle \right],\end{aligned} \tag{7.15}$$

where the notation

$$\begin{aligned}\langle l \underline{K}, m | v | l' \underline{K}, m' \rangle &= \int \phi^* (\underline{k}_l + \underline{K}, \underline{r}_1) \phi^* (\underline{k}_m, \underline{r}_2) v_{12} \phi (\underline{k}_{l'} + \underline{K}, \underline{r}_1) \\ &\qquad \phi (\underline{k}_{m'}, \underline{r}_2) \, d\tau_{12}\end{aligned}$$

has been used.

The evaluation of $\langle \phi_{\lambda \underline{K}} | H | \phi_{\mu \underline{K}} \rangle$ requires more care. From (7.13)

$$\langle \phi_{\lambda \underline{K}} | H | \phi_{\mu \underline{K}} \rangle = n^{-1} \sum_{s}^{(\lambda)} \sum_{t}^{(\mu)} \langle \theta_\lambda(\underline{k}_s, \underline{k}_s + \underline{K}) | H | \theta_\mu(\underline{k}_t, \underline{k}_t + \underline{K}) \rangle \qquad (7.16)$$

and if Ψ_λ, Ψ_μ are given by (7.8) and (7.9) the only non-zero contributions to this sum occur when

(i) $t = s$ (n possibilities)

(ii) $s = l$ or m, $t = l'$ or m'

The contribution of case (i) to (7.16) is

$$\frac{n-2}{n} \langle \Psi_\lambda | H | \Psi_\mu \rangle$$

and the contributions from case (ii) are

(a) $s = l$, $t = l'$ $\quad n^{-1} \langle l \underline{K}, m | v | l' \underline{K}, m' \rangle$

(b) $s = l$, $t = m'$ $\quad - n^{-1} \langle l \underline{K}, m | v | m' \underline{K}, l' \rangle$

(c) $s = m$, $t = m'$ $\quad n^{-1} \langle l, m \underline{K} | v | l', m' \underline{K} \rangle$

(d) $s = m$, $t = l'$ $\quad - n^{-1} \langle l, m \underline{K} | v | m', l' \underline{K} \rangle$

Thus

$$\begin{aligned} \langle \phi_{\lambda \underline{K}} | H | \phi_{\mu \underline{K}} \rangle - \langle \Psi_\lambda | H | \Psi_\mu \rangle &= n^{-1} \big[\langle l \underline{K}, m | v | l' \underline{K}, m' \rangle - \langle l \underline{K}, m | v | m' \underline{K}, l' \rangle \\ &\quad + \langle l, m \underline{K} | v | l', m' \underline{K} \rangle - \langle l, m \underline{K} | v | m', l' \underline{K} \rangle \\ &\quad - 2 \langle lm | v | l'm' \rangle + 2 \langle lm | v | m'l' \rangle \big] \end{aligned} \qquad (7.17)$$

From (7.14), (7.15) and (7.17) it is not difficult to see that, for a given direction of $\underline{K}$, (7.14) is an even function of K as long as one condition is fulfilled. This is that for each $\psi_\lambda = \Delta(\underline{k}_1, \ldots \underline{k}_n)$ appearing in (7.4) with a coefficient a_λ there appears a

$$\psi_{\lambda'} = \Delta(-\underline{k}_1, \ldots -\underline{k}_n)$$

with a coefficient $\pm a_\lambda$ (The sign must be the same for all λ). It may be shown that this is the case if Ψ is non-degenerate and the crystal has a centre of inversion. Thus in this case (7.14) is of the form $\mathcal{E} + C_0 K^2$ for small K. It follows that a state with one reversed spin and wave-vector $\underline{K}$ must exist with an energy not greater than this. Also if the metal is ferromagnetic the energy of such a state must lie above the ground-state energy $\mathcal{E}$. Hence states of the type considered exist with energies of the form (7.3) where $C < C_0$. This completes the proof of the existence of spin-wave states.

25. Method of calculating spin wave energies

It is the object of this section to present a method which may, in principle, be used to calculate spin wave energies accurately. The equations obtained form a generalization of equations given by Herring

(1952 b) although the method of derivation is quite different. It is assumed that the ground state wave function Ψ is known i.e. that the coefficients a_λ in (7.4) are known. In a practical calculation one could normally only find approximations to Ψ but the spin-wave energies should not depend too critically on its exact form.

The method used here is to expand the exact spin wave function $\Phi_{\underline{K}}$ as a linear combination of determinants.

$$\Delta(\underline{k}_1, \ldots \underline{k}_{n-1} \; ; \; \underline{q} + \underline{K}), \tag{7.18}$$

where the wave-vector $\underline{q} + \underline{K}$ after the semicolon represents a state of β spin, and

$$\sum_{t=1}^{n-1} \underline{k}_t + \underline{q} = \underline{L}.$$

If the state of spin α and wave vector $\underline{q}_t$ is unoccupied in (7.18), then the determinant is just $\theta_\lambda(\underline{q}, \; \underline{q} + \underline{K})$ where θ_λ is derived in the previously described manner from

$$\Psi_\lambda = \Delta(\underline{k}_1, \ldots \underline{q}_t, \ldots \underline{k}_{n-1}).$$

However if the state of spin α and wave-vector $\underline{q}$ is occupied in (7.18) then the determinant is not equal to any of the functions θ_λ and new functions must be defined. A typical one is

$$\eta_\nu(\underline{K}) = \Delta(\underline{k}_1, \ldots \underline{k}_t \ldots \underline{k}_{n-1} \; ; \; \underline{k}_t + \underline{K}). \tag{7.19}$$

For the single-band model considered the functions $\theta_\lambda(\underline{q}, \underline{q}+\underline{K})$ and $\eta_\nu(\underline{K})$ form a complete set in which to expand $\Phi_{\underline{K}}$. It will be assumed that the coefficients in this expansion may be expanded in powers of K, for a given direction of $\underline{K}$, and the zero order terms are known since $\Phi_0 = \Theta_0$. Thus

$$\Phi_{\underline{K}} = n^{-\frac{1}{2}} \sum_\lambda \sum_s^{(\lambda)} (a_\lambda + b_{\lambda s} K + c_{\lambda s} K^2 + \ldots) \theta_\lambda(\underline{k}_s, \underline{k}_s + \underline{K}) + \sum_\nu (d_\nu K + e_\nu K^2 + \ldots) \eta_\nu(\underline{K}) \tag{7.20}$$

where the coefficients $b_{\lambda s}$, $a_{\lambda s}$, d_ν are to be determined. On substituting in the Schrödinger equation

$$H \Phi_{\underline{K}} = E(\underline{K}) \Phi_{\underline{K}} , \tag{7.21}$$

multiplying by $\langle \theta_\mu(\underline{k}_t, \underline{k}_t + \underline{K}) |$ and $\langle \eta_\mu(\underline{K}) |$, and expanding $E(\underline{K})$ in the form (7.3), one obtains a set of equations which may be broken down by expanding the matrix elements in Maclaurin's series in K and equating coefficients of different powers of K. Equating coefficients of K yields

$$\left[\frac{\partial}{\partial K} \langle \theta_\mu(\underline{k}_t, \underline{k}_t + \underline{K}) | H | \Theta_{\underline{K}} \rangle \right]_{K=0} + n^{-\frac{1}{2}} \sum_\lambda \sum_s^{(\lambda)} b_{\lambda s} \langle \theta_\mu(\underline{k}_t, \underline{k}_t) | H - \mathcal{E} | \theta_\lambda(\underline{k}_s, \underline{k}_s) \rangle + \sum d_\nu \langle \theta_\mu(\underline{k}_t, \underline{k}_t) | H | \eta_\nu(0) \rangle = 0 \tag{7.22}$$

and

$$\left[\frac{\partial}{\partial K}\langle \eta_\mu(\underline{K})|H|\Theta_{\underline{K}}\rangle\right]_{K=0}$$
$$+ n^{-\frac{1}{2}}\sum_\lambda\sum_s{}^{(\lambda)} b_{\lambda s}\langle \eta_\mu(0)|H|\theta_\lambda(\underline{k}_s,\underline{k}_s)\rangle$$
$$+\sum_\nu d_\nu\langle \eta_\mu(0)|H-\varepsilon|\eta_\nu(0)\rangle$$
$$= 0 . \qquad (7.23)$$

Equating coefficients of K^2 gives

$$\tfrac{1}{2}\left[\frac{\partial^2}{\partial K^2}\langle \theta_\mu(\underline{k}_t,\underline{k}_t+\underline{K})|H|\Theta_{\underline{K}}\rangle\right]_{K=0}$$
$$+ n^{-\frac{1}{2}}\sum_\lambda\sum_s{}^{(\lambda)}\Big\{b_{\lambda s}\left[\frac{\partial}{\partial K}\langle \theta_\mu(\underline{k}_t,\underline{k}_t+\underline{K})|H|\theta_\lambda(\underline{k}_s,\underline{k}_s+\underline{K})\rangle\right]_{K=0}$$
$$+ c_{\lambda s}\langle \theta_\mu(\underline{k}_t,\underline{k}_t)|H-\varepsilon|\theta_\lambda(\underline{k}_s,\underline{k}_s)\rangle\Big\}$$
$$+\sum_\nu\Big\{d_\nu\left[\frac{\partial}{\partial K}\langle \theta_\mu(\underline{k}_t,\underline{k}_t+\underline{K})|H|\eta_\nu(K)\rangle\right]_{K=0}$$
$$+ e_\nu\langle \theta_\mu(\underline{k}_t,\underline{k}_t)|H|\eta_\nu(0)\rangle\Big\}$$
$$= n^{-\frac{1}{2}} q_\mu C . \qquad (7.24)$$

The eigenvalue problem has now been removed; (7.23) and (7.25) are a set of linear equations which determine the $b_{\lambda s}$ and d_ν. C is obtained in terms of these coefficients by multiplying (7.24) by $n^{-\frac{1}{2}}a^*_\mu$ and carrying out the summation $\sum_\mu\sum_t{}^{(\mu)}$.

Then

$$C = \tfrac{1}{2}\left[\frac{\partial^2}{\partial K^2}\langle \Theta_{\underline{K}}|H|\Theta_{\underline{K}}\rangle\right]_{K=0}$$
$$+ n^{-\frac{1}{2}} \sum_{\lambda} \sum_{s}^{(\lambda)} b_{\lambda s}\left[\frac{\partial}{\partial K}\langle \Theta_{\underline{K}}|H|\theta_{\lambda}(\underline{k}_s, \underline{A}_s + \underline{K})\rangle\right]_{K=0}$$
$$+ \sum_{\nu} d_{\nu}\left[\frac{\partial}{\partial K}\langle \Theta_{\underline{K}}|H|\eta_{\nu}(\underline{K})\rangle\right]_{K=0} . \qquad (7.25)$$

Actually (7.22) and (7.23) do not determine the $b_{\lambda s}$ uniquely since it is clear that the equations remain unaltered if $b_{\lambda s} \to b_{\lambda s} + \alpha a_{\lambda}$ where α is a constant. However the normalization condition on $\Phi_{\underline{K}}$ gives

$$n^{-1} \sum_{\lambda} \sum_{s}^{(\lambda)} |a_{\lambda} + b_{\lambda s} K + \ldots|^2 + \sum_{\nu} |d_{\nu} K + \ldots|^2 = 1$$

and equating coefficients of K one finds that

$$\mathrm{Re} \sum_{\lambda} \sum_{s}^{(\lambda)} a_{\lambda}^{*} b_{\lambda s} = 0 . \qquad (7.26)$$

This condition serves to define the $b_{\lambda s}$ uniquely.

An attempt may be made to solve equations (7.22) and (7.23) iteratively. Thus if one first places all $b_{\lambda s}$ except $b_{\mu t}$ equal to zero and all d_{ν} except d_{μ} equal to zero one may solve for $b_{\mu t}$ and d_{μ}. These values may then be put back in the equations and these solved again for $b_{\mu t}$ and d_{μ} and the process repeated

indefinitely.

One obtains

$$b_{\mu t} = -n^t \frac{\left[\frac{\partial}{\partial K} \langle \theta_\mu(\underline{k}_t, \underline{k}_t + \underline{K}) | H | \Theta_{\underline{K}} \rangle\right]_{K=0}}{\langle \theta_\mu(\underline{k}_t, \underline{k}_t) | H | \theta_\mu(\underline{k}_t, \underline{k}_t) \rangle - \xi} + \cdots$$

$$d_\mu = -\frac{\left[\frac{\partial}{\partial K} \langle \eta_\mu(K) | H | \Theta_{\underline{K}} \rangle\right]_{K=0}}{\langle \eta_\mu(0) | H | \eta_\mu(0) \rangle - \xi} + \cdots \qquad (7.27)$$

If these series are substituted in (7.25) a series is obtained for C which is identical with the coefficient of F^2 in (21) of Edwards (1962), although slightly different functions are used there. This method may be of little practical value since even if the series converges the convergence may well be slow.

25.1 Evaluation of matrix elements

Although it has not yet proved possible to solve (7.22) and (7.25) in a very general case it is advisable to evaluate the matrix elements involved for future reference. In particular it must be verified that the matrix elements can be expanded in powers of K. From (7.12), (7.13) and (7.11) one obtains

$$\begin{aligned}
&\langle \theta_\mu(\underline{k}_t, \underline{k}_t+\underline{K}) | H | \Phi_{\underline{K}} \rangle n^{1/2} \\
&\quad = a_\mu \{ \varepsilon + w_r(\underline{k}_t+\underline{K}) - w_r(\underline{k}_t) \\
&\qquad + \sum_s{}^{(\nu)} [\langle s, t\underline{K} | v | s, t\underline{K} \rangle - \langle st | v | st \rangle \\
&\qquad\quad - \langle s, t\underline{K} | v | t, s\underline{K} \rangle + \langle st | v | ts \rangle] \} \\
&+ \sum_{\lambda \neq \mu} a_\lambda \{ \delta_{tl'} [\langle m', l'\underline{K} | v | m, l\underline{K} \rangle - \langle m'l' | v | ml \rangle \\
&\qquad - \langle m', l'\underline{K} | v | l, m\underline{K} \rangle + \langle m'l' | v | lm \rangle] \\
&\qquad + \delta_{tm'} [\langle l', m'\underline{K} | v | l, m\underline{K} \rangle - \langle l'm' | v | lm \rangle \\
&\qquad\quad - \langle l', m'\underline{K} | v | m, l\underline{K} \rangle + \langle l'm' | v | ml \rangle] \}
\end{aligned} \tag{7.28}$$

where as before l, m, l', m' denote the wave-vectors of the one-electron functions by which ψ_λ and ψ_μ differ. On putting

$$b(\underline{k}, \underline{r}) = \exp(i\underline{k}\cdot\underline{r})\, u(\underline{k}, \underline{r}) \tag{7.29}$$

a typical integral in (7.28) becomes

$$\begin{aligned}
&\langle m', l'\underline{K} | v | m, l\underline{K} \rangle \\
&\quad = \int \exp\{ i [(\underline{k}_m - \underline{k}_{m'})\cdot \underline{r}_1 + (\underline{k}_l - \underline{k}_{l'})\cdot \underline{r}_2] \} \\
&\qquad u^*(\underline{k}_{m'}, \underline{r}_1)\, u^*(\underline{k}_{l'}+\underline{K}, \underline{r}_2)\, u(\underline{k}_m, \underline{r}_1)\, u(\underline{k}_l+\underline{K}, \underline{r}_2) \\
&\qquad\qquad d\tau_{1,2}
\end{aligned}$$

and there is no difficulty in expanding in powers of K since $u(\underline{k}, \underline{r})$ is a well-behaved function of $\underline{k}$. The coefficient of K which appears in (7.22) is, therefore, easily determined.

Further matrix elements which appear in (7.22) are

$$\begin{aligned}
&\langle \theta_\mu(\underline{k}_t, \underline{k}_t) | H | \theta_\mu(\underline{k}_t, \underline{k}_t) \rangle \\
&\qquad = E_\mu + \sum_{s \neq t}{}^{(\mu)} \langle ts | v | st \rangle
\end{aligned} \tag{7.30}$$

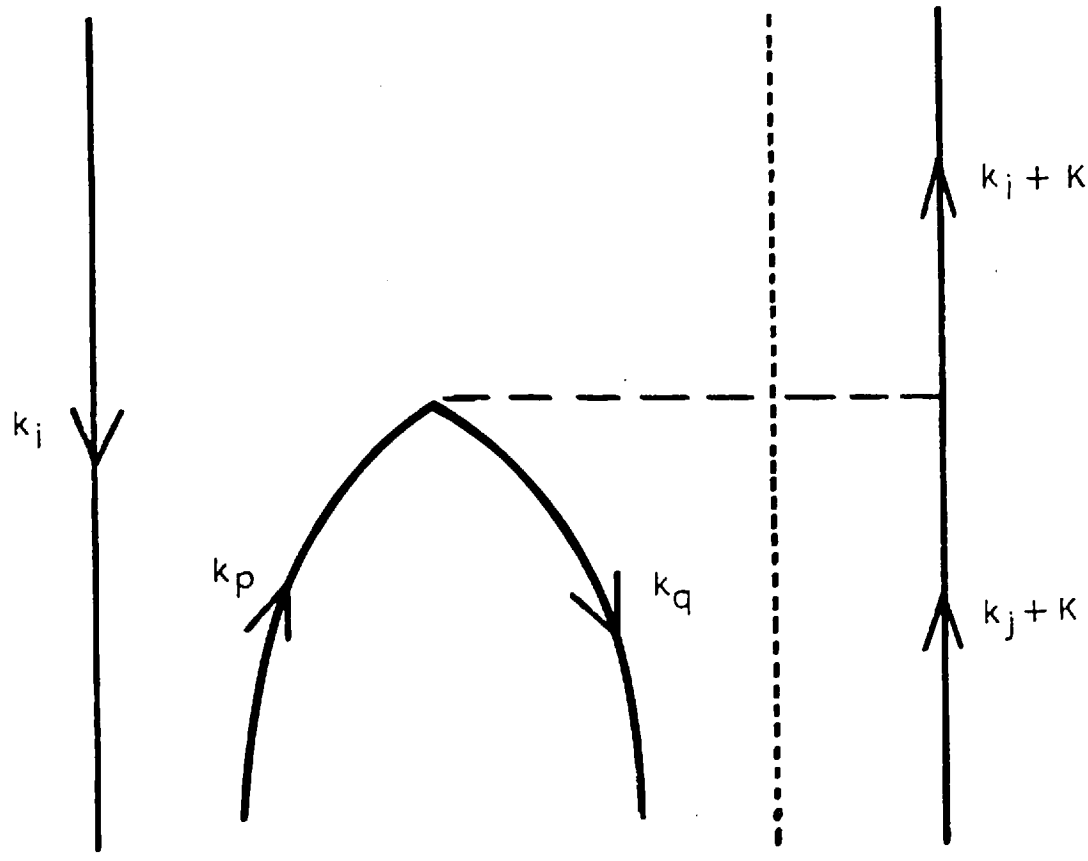

FIGURE 21

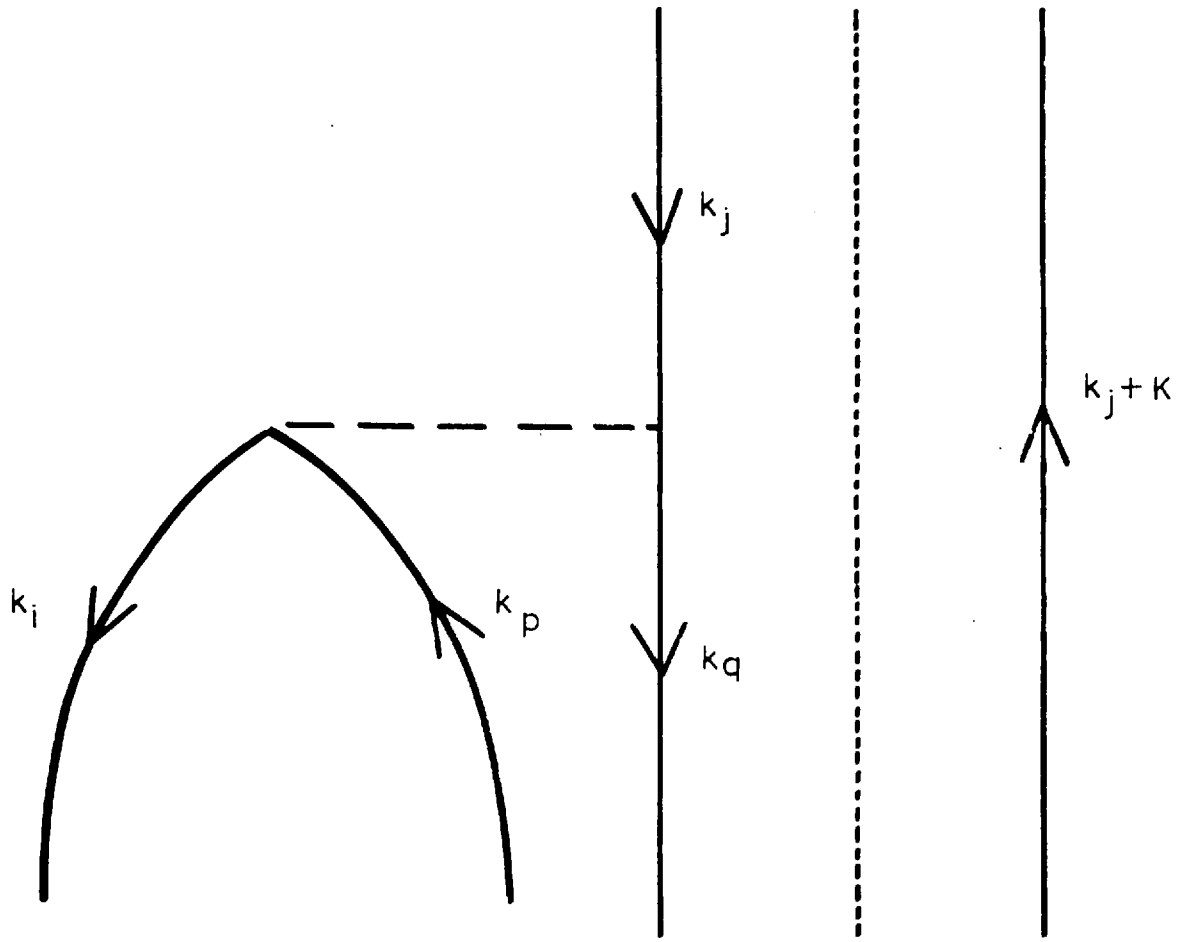

FIGURE 22

and for $s \neq t$

$$\langle \theta_\mu(\underline{k}_t, \underline{k}_v) | H | \theta_\mu(\underline{k}_s, \underline{k}_s) \rangle = - \langle ts | v | st \rangle . \tag{7.31}$$

Also for $\lambda \neq \mu$ and $t \neq l'$ or m'

$$\langle \theta_\mu(\underline{k}_t, \underline{k}_t) | H | \theta_\lambda(\underline{k}_t, \underline{k}_t) = \langle l'm' | v | lm \rangle - \langle m'l' | v | lm \rangle \tag{7.32}$$

and for $\lambda \neq \mu$ and $s \neq t$

$$\begin{aligned} \langle \theta_\mu(\underline{k}_t, \underline{k}_t) | H | \theta_\lambda(\underline{k}_s, \underline{k}_s) \rangle &= (\delta_{sl} \delta_{tl'} + \delta_{sm} \delta_{tm'}) \langle l'm' | v | lm \rangle \\ &\quad - (\delta_{sl} \delta_{tm'} + \delta_{sm} \delta_{tl'}) \langle m'l' | v | lm \rangle . \end{aligned} \tag{7.33}$$

It remains to examine matrix elements involving the functions $\eta_\nu(\underline{K})$. A typical $\eta_\nu(\underline{K})$ is represented as the initial state in the diagrams of figures 21 and 22 which are diagrams of the type used by Goldstone (1957) referred to a state Ψ_λ as vacuum state. Lines representing states of spin α and spin β are drawn to the left and right respectively of the vertical dotted lines. The diagrams correspond to matrix elements

$$\langle \theta_\lambda(\underline{k}_s, \underline{k}_s + \underline{k}) | v | \eta_\nu(\underline{K}) \rangle \tag{7.34}$$

with s = i and s = j. The only other non-zero matrix element (7.34) is that with s = q and is represented by figure 21 with i and q interchanged. The values of these matrix elements are as follows:

$$\langle \theta_\lambda(\underline{k}_i, \underline{k}_i+\underline{K})|v|\eta_\nu(\underline{K})\rangle = \langle q,i\underline{K}|v|p,j\underline{K}\rangle$$

$$\langle \theta_\lambda(\underline{k}_j, \underline{k}_j+\underline{K})|v|\eta_\nu(\underline{K})\rangle = \langle iq|v|pj\rangle - \langle qi|v|pj\rangle$$

$$\langle \theta_\lambda(\underline{k}_q, \underline{k}_q+\underline{K})|v|\eta_\nu(\underline{K})\rangle = -\langle i,q\underline{K}|v|p,j\underline{K}\rangle \quad (7.35)$$

In (7.23) the matrix element

$$\langle \eta_\mu(\underline{K})|H|\Theta_{\underline{K}}\rangle = n^{-\frac{1}{2}} \sum_\lambda \sum_s{}^{(\lambda)} q_\lambda \langle \eta_\mu(\underline{K})|H|\theta_\lambda(\underline{k}_s, \underline{k}_s+\underline{K})\rangle \quad (7.36)$$

to the sum (7.36)

appears and from (7.35) the contribution of a particular λ is of the form

$$\langle p,j\underline{K}|v|q,i\underline{K}\rangle - \langle pj|v|qi\rangle$$
$$-\langle p,j\underline{K}|v|i,q\underline{K}\rangle + \langle pj|v|iq\rangle .$$

This expression is easily expanded in powers of K, so the coefficient

of K in (7.36), which appears in (7.23), is easily calculated.

The remaining matrix elements $\langle \eta_\mu(0) | H | \eta_\nu(0) \rangle$ may be calculated in particular cases without difficulty.

24. Spin wave energies in special cases

Existing formal calculations of spin wave energies in metals are those of Herring (1952b) and Izuyama (1960). Both these calculations are based on the same approximation and they may be regarded as special cases of the general method presented in the previous section. It is of interest to confirm their results using this direct method.

24.1 Herring's approximation

In the notation of the previous chapter Herring's approximation is equivalent to assuming that the ground state may be represented by a single determinant Ψ_0 and that a spin-wave state may be approximated by a linear combination of determinants $\theta_0(\underline{k}, \underline{k} + \underline{K})$. Thus $\Sigma = E_0, a_0 = 1$, $a_\lambda = 0$ for $\lambda \neq 0$ and all terms involving η_ν must be omitted. The results of section 23 must be slightly modified since the one-electron functions of Herring's paper ϕ_λ are not those defined in (7.2) but solutions of the Hartree-Fock equations. The required modifications are that all matrix elements must be calculated using the Hartree-Fock one-electron functions and that the one-electron energies $w(\underline{k}_1)$ and $w(\underline{k}_1 + \underline{K})$, corresponding to α and β spin states

respectively, must be expressed in terms of Hartree-Fock energies $\lambda_\alpha(\underline{k}_\lambda)$, $\lambda_\rho(\underline{k}_\lambda+\underline{K})$ as follows:

$$\omega(\underline{k}_\lambda) = \lambda_\alpha(\underline{k}_\lambda) - \sum_s^{(\omega)} [\langle \lambda s|v|\lambda s\rangle - \langle \lambda s|v|s\lambda\rangle]$$

$$\omega(\underline{k}_\lambda+\underline{K}) = \lambda_\rho(\underline{k}_\lambda+\underline{K}) - \sum_s^{(\omega)} \langle \lambda \underline{K},s|v|\lambda \underline{K},s\rangle . \qquad (7.37)$$

The link between the notation of this paper and that of Herring is that Herring's matrix element $\underline{\Phi}_{\lambda\mu}(\underline{K})$ is given by

$$\underline{\Phi}_{\lambda\mu}(\underline{K}) = \delta_{\lambda\mu}[\lambda_\rho(\underline{k}_\lambda+\underline{K}) - \lambda_\alpha(\underline{k}_\mu)] - \langle \lambda\underline{K},\mu|v|\mu\underline{K},\lambda\rangle$$

$$= \langle \theta_0(\underline{k}_\lambda, \underline{k}_\lambda+\underline{K})|H-E_0|\theta_0(\underline{k}_\mu,\underline{k}_\mu+\underline{K})\rangle . \qquad (7.38)$$

As in Herring's paper let

$$\underline{\Phi}_{\lambda\mu}(\underline{K}) = \underline{\Phi}^0_{\lambda\mu} + K\underline{\Phi}'_{\lambda\mu} + K^2\underline{\Phi}''_{\lambda\mu} + \ldots \qquad (7.39)$$

for a given direction of $\underline{K}$; then (7.32) becomes

$$\sum_\mu \underline{\Phi}^0_{\lambda\mu}\underline{e}_\mu + \sum_\mu \underline{\Phi}'_{\lambda\mu} = 0 \qquad (7.40)$$

which is exactly Herring's equation (18) and (7.36) gives

$$\sum_j \ell_{ij} = 0 \,. \tag{7.41}$$

From (7.20) the wave function of the spin-wave state is

$$\Psi_{\underline{K}} = n^{-\frac{1}{2}} \sum_j (1 + \ell_{ij} K + \ldots)\, \theta_0(\underline{k}_j, \underline{k}_j + \underline{K}) \tag{7.42}$$

and, from (7.39), (7.25) and (7.40), its energy is

$$E(K) = E_0 + n^{-1} K^2 \sum_{i,j} \left[\Phi''_{ij} + \ell_{ij} \Phi'_{ji} \right]$$

$$= E_0 + n^{-1} K^2 \sum_{i,j} \left[\Phi''_{ij} - \ell^*_{ij} \Phi^0_{ji} \ell_{ji} \right] \tag{7.43}$$

which is just Herring's equation (42). All of Herring's (1952b) results on the spin wave states are therefore simply derived by the present method.

24.2 Izuyama's model

Izuyama (1960) used field theoretical methods to show how to

calculate spin wave energies approximately for a model which in one respect is more general than that of Herring. His essential approximation (the "ladder" approximation) is entirely equivalent to Herring's, but he considers the case in which the ground state is not necessarily the one of complete spin alinement. It seems worthwhile to show that Izuyama's results are simply derived by the present method.

Izuyama considers a system with the Hamiltonian

$$H = \sum_{\underline{k},\sigma} w(\underline{k})\, n_{\underline{k}\sigma} + \frac{1}{2} \sum_{\underline{k}\neq 0} J(\underline{k})\, \rho_{\underline{k}}\, \rho_{-\underline{k}} \qquad (7.44)$$

where $n_{\underline{k}\sigma}$ and $\rho_{\underline{k}}$ are given by

$$n_{\underline{k}\sigma} = q^{*}_{\underline{k}\sigma}\, q_{\underline{k}\sigma}$$

and

$$\rho_{\underline{k}} = \sum_{\underline{l},\sigma} q^{*}_{\underline{l}+\underline{k},\sigma}\, q_{\underline{l}\sigma} \,,$$

$a_{\underline{k}\sigma}$ being the destruction operator for the state of wave-vector $\underline{k}$ and spin σ. Izuyama denotes the one-electron energies by $E(\underline{k})$ but they are here denoted by $w(\underline{k})$ to conform with previous notation. Apart from a constant (7.44) may be written

$$H = \sum_{\underline{k},\sigma} \omega(\underline{k})\, n_{\underline{k}\sigma} + \tfrac{1}{2} \sum_{\underline{k}\neq 0} J(\underline{k}) \sum_{\underline{l},\sigma} \sum_{\underline{l}',\sigma'} a^{*}_{\underline{l}+\underline{k},\sigma}\, a^{*}_{\underline{l}'-\underline{k},\sigma'}\, a_{\underline{l}'\sigma'}\, a_{\underline{l}\sigma} ,$$

and this is just the Hamiltonian for a system of interacting fermions with one-electron energies $w(\underline{k})$, one-electron functions $b(\underline{k}, \underline{r})$, and interactions v_{ij} such that

$$\int \phi^{*}(\underline{l}+\underline{k}, \underline{r}_1)\, \phi^{*}(\underline{l}'-\underline{k}, \underline{r}_2)\, v_{12}\, \phi(\underline{l}, \underline{r}_1)\, \phi(\underline{l}', \underline{r}_2)\, d\tau_{12} = J(\underline{k}) . \qquad (7.45)$$

The assumption that J is a function of $\underline{k}$ only holds for free electrons and Izuyama only considers in detail the case where $w(\underline{k})$ is also appropriate to free electrons. It is assumed that the ground state of the system is one in which one-electron levels are filled as shown in figure 13. Suppose there are N_α states of spin α occupying the region $k < k_{F\alpha}$ and N_β states of spin β occupying the region $k < k_{F\beta}$. (α and β are interchanged in Izuyama's notation). The ground state is represented by the appropriate Slater determinant ψ_0 and, the wave-function for a spin-wave state may be written

as

$$\Phi_{\underline{K}} = [n(\underline{K})]^{-\frac{1}{2}} \sum_s{}^{\S} \theta_0(\underline{k}_s, \underline{k}_s + \underline{K})\,(1 + \epsilon_s K) \tag{7.46}$$

for small $\underline{K}$ where $\sum^{\S}$ denotes summation over the $n(\underline{K})$ wave-vectors $\underline{k}_s$ which are such that $|\underline{k}_s| \leq k_{F\alpha}$ and $|\underline{k}_s + \underline{K}| > k_{F\beta}$.
The equation corresponding to (7.32) is

$$\sum_s{}^{\S} \left[\frac{\partial}{\partial K} \langle \theta_0(\underline{k}_t, \underline{k}_t + \underline{K}) | H | \theta_0(\underline{k}_s, \underline{k}_s + \underline{K}) \rangle \right]_{K=0}$$
$$+ \sum_s{}^{\S} \epsilon_s \langle \theta_0(\underline{k}_t, \underline{k}_t) | H - E_0 | \theta_0(\underline{k}_s, \underline{k}_s) \rangle = 0 \tag{7.47}$$

and the spin-wave energy is given by

$$E_0 + CK^2$$

for small K where, corresponding to (7.35),

$$C = \frac{1}{2n} \sum_s{}^{\S} \sum_t{}^{\S} \left[\frac{\partial^2}{\partial K^2} \langle \theta_0(\underline{k}_s, \underline{k}_s + \underline{K}) | H | \theta_0(\underline{k}_t, \underline{k}_t + \underline{K}) \rangle \right]_{K=0}$$
$$+ \frac{1}{n} \sum_s{}^{\S} \sum_t{}^{\S} \epsilon_t \left[\frac{\partial}{\partial K} \langle \theta_0(\underline{k}_s, \underline{k}_s + \underline{K}) | H | \theta_0(\underline{k}_t, \underline{k}_t + \underline{K}) \rangle \right]_{K=0}. \tag{7.48}$$

The matrix elements are simple to evaluate and, using the free electron expression

$$w(\underline{k}) = \hbar^2 k^2 / 2m \ ,$$

(7.47) and (7.48) become

$$-\frac{\hbar^2}{m} k_{tz} = \sum_s{}^{+} J(\underline{k}_t - \underline{k}_s)(\rho_t - \rho_s) \tag{7.49}$$

and

$$C = \frac{\hbar^2}{2m} \frac{N_\alpha + N_\beta}{N_\alpha - N_\beta} + \frac{\hbar^2}{m} \cdot \frac{1}{N_\alpha - N_\beta} \sum_s{}^{+} k_{sz} \rho_s \tag{7.50}$$

where k_{tz} is the component of $\underline{k}_t$ in the direction of $\underline{K}$ and Σ^+ denotes summation over wave-vectors $\underline{k}_s$ such that $|\underline{k}_s| \leq k_{F\alpha}$ and $|\underline{k}_s| > k_{F\beta}$.

Equations (7.49) and (7.50) are identical with Iguyama's equations (16) and (17).

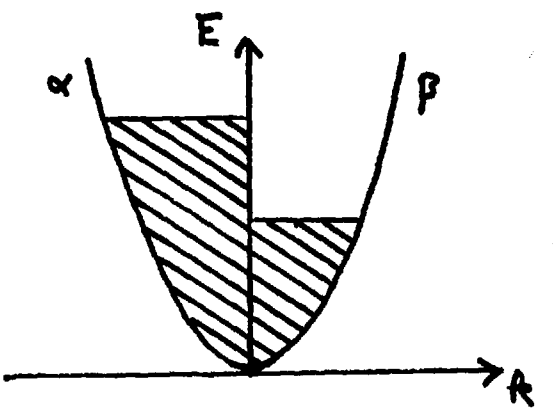

Fig. 23

25. Discussion

The general equations for spin-wave energies given in section 23 have not yet been solved for any particular case and the difficulties

are considerable. However, Herring (1952 a,b) has been able to solve the simpler equations of section 24.1 in the case of free electrons and in a case with constant exchange integral between Bloch functions. It has been pointed out earlier that a constant exchange integral results from a short range interaction and that a model based on this interaction may serve to justify the conventional collective electron treatment of the band-type states. Spin-wave energies in this model are therefore of interest. In the notation of this chapter Herring's results for cubic crystals may be written

$$E(\underline{K}) - E_0 = (6n)^{-1} K^2 \sum_{\underline{k}}^{(0)} \left\{ \nabla^2 \omega(\underline{k}_\lambda) - \frac{2N}{nI_0} |\nabla \omega(\underline{k}_\lambda)|^2 \right\}, \tag{7.51}$$

where I_0 is essentially the coulomb repulsion integral for two electrons on the same atom. It is interesting to note that spin-wave energies depend strongly on the band structure. The first term in (7.51) is proportional to the effective mass averaged over the portion of the band occupied by carriers in the ground state. Equation (7.51) gives spin-wave energies of the right order of magnitude, but a detailed comparison with experiment is not really possible.

Finally it may be pointed out that the band theory of spin waves has removed the difficulties in interpreting data which have sometimes been experienced (see e.g. Hofmann et al 1956) due to

non-integral magneton numbers. Formulae such as (6.25) and (6.26) do not depend on a localized model. However marked discrepancies occur between spin-wave energies deduced from the $T^{3/2}$ laws of magnetization and specific heat, neutron diffraction measurements and spin wave resonance experiments.

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Spin waves in ferromagnetic metals

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A qualitative discussion is given of the low-lying states of a ferromagnetic metal and the consequent low-temperature thermodynamic properties of the system. It is concluded that a typical low-lying state differs from the ground state by a number of independent particle excitations, such as are considered in Stoner's collective electron theory, and a number of exciton-like excitations, in which an electron of minority spin is bound to a hole of majority spin, which correspond to spin waves. The low temperature specific heat and the deviation of the magnetization from saturation may then both be expressed as the sum of two terms, one typical of collective electron theory and one of spin wave theory. A formal proof is given of the existence of spin waves of long wavelength in metals and a general method of calculating their energies is outlined. Herring's results on spin-wave energies are obtained as a special case.

1. Introduction

Most of the existing theoretical work on spin waves is based either on the phenomenological approach introduced by Lifshitz (1945) and Herring & Kittel (1951), or on a spin-Hamiltonian approach which has its roots in the Heitler–London model. Applications of the latter approach have been reviewed by Van Kranendonk & Van Vleck (1958) and they stress the limited validity of the method. Although a localized-spin model may apply to non-conducting ferromagnetics such as ferrites and garnets, and perhaps to the rare earth metals, it cannot apply to the transition metals in which there are a non-integral number of unpaired spins per lattice site. The phenomenological approach, on the other hand, is independent of any detailed model and it has proved very successful for discussing ferromagnetic resonance and allied effects, both in insulators and metals.* However, this approach leaves many problems unsolved. For example, it is not well adapted to discussing the thermodynamic properties of a ferromagnetic metal since it does not yield the complete energy spectrum of the system. In particular it throws no light on the relation between spin-wave theory and collective electron theory (Stoner 1948; Wohlfarth 1953). Also, all results derived by the phenomenological method contain the exchange stiffness constant as a parameter and this can only be determined theoretically by a quantum-mechanical calculation which is equivalent to calculating spin-wave energies. This paper is concerned with these problems which have only been discussed previously in any detail by Herring & Kittel (1951) and Herring (1952*a*,*b*), to be referred to as H.K., H (*a*), H (*b*), respectively, and Izuyama (1960). The present work, although employing quite different methods, is closely related to the work of these authors and it is convenient to end this introduction by summarizing first their results and then the results of this paper.

In H.K. a ferromagnetic metal is considered whose ground state has total wave vector $\mathbf{K} = 0$ and total spin S'. It is assumed that there exists a macroscopic

* A recent review is by Akhiezer, Bar'Yakhtar & Kaganov (1960).

exchange energy proportional to the square of the rate at which the direction of magnetization changes with position, and it is hence shown that states of small K and total spin $S'-1$ exist with energies $O(K^2)$ above the ferromagnetic ground state. These states are identified as spin waves and in H (b) it is shown how to calculate their energies, within a certain approximation, by the indirect method of considering the response of the saturated specimen to a small perturbing magnetic field. In H.K. it is surmised that the low-energy states of a ferromagnetic metal are of two types: the band-type states of collective electron theory with 'no spin waves excited' and states derived from these by excitation of spin waves. It is further conjectured that the contributions of collective electron and spin-wave excitations to the specific heat may be additive. Izuyama (1960) has used field theoretical methods to calculate spin wave energies within the same approximation as Herring.

The purpose of the present paper is to attempt to place some of the conjectures made in H.K. on a firmer foundation and to describe a method of calculating spin-wave energies in metals which should be capable of greater accuracy than has hitherto been achieved. This method is closer to that used by Slater (1937) in his calculation for a ferromagnetic insulator than to the method of H (b). For simplicity the work of the present paper is restricted to a single-band model of a metal although there is little doubt that the qualitative results of § 2 hold even in the case of several overlapping bands. Section 2 is devoted to a qualitative discussion of the low-energy states of a ferromagnetic metal and the consequent low temperature thermodynamic properties of the system. It is concluded that the low temperature specific heat may be expressed as the sum of two terms, one of which may be calculated by collective electron theory and the other by normal spin-wave theory. A similar conclusion is reached concerning the deviation of the magnetization from saturation at low temperatures. In § 3 it is shown formally, assuming only the convergence of a certain perturbation series, that spin waves of long wavelength exist in metals and a method of calculating their energies is described. Some special applications of this method are discussed in § 4 and the results of H (b) are derived in a direct manner. The possibility of calculating spin-wave energies to a higher approximation than that of H (b) is considered. As in H (b) magnetic and spin-orbit interactions are neglected throughout the paper.

2. The low-temperature thermodynamic properties of a ferromagnetic metal

The specific heat and magnetization of a ferromagnetic metal at low temperatures are determined by the energy distribution of the lowest stationary states of the system. The discussion of these states which follows is based on a band description of the metal although correlation effects are considered. Thus in general an eigenfunction of the system may be written as a linear combination of Slater determinants formed from one-electron functions $b(\mathbf{k}, \mathbf{r}_i)\alpha(i)$ and $b(\mathbf{k}, \mathbf{r}_i)\beta(i)$, where $\mathbf{r}_i$ is the position of the ith electron, $b(\mathbf{k}, \mathbf{r}_i)$ is a Bloch function with wave vector $\mathbf{k}$ and $\alpha(i)$, $\beta(i)$ are the eigenfunctions of σ_{iz}, the z component of spin of the ith electron, with eigenvalues $+\frac{1}{2}$ and $-\frac{1}{2}$, respectively.*

* Spin is measured throughout in units of $\hbar$.

Consider a model which consists of $2N-n$ electrons in a single band containing N states of each spin, where $n < N$, and assume that the ground state of the system is that of maximum multiplicity with total spin S' equal to $\frac{1}{2}n$. At first only the low-lying states of the system with S' equal to $\frac{1}{2}n$ or $\frac{1}{2}n-1$ will be discussed and it is sufficient to consider those states which have S' and the z component of spin S'_z equal. Suppose ψ is the eigenfunction of such a state; then if S_x, S_y are x and y components of spin the functions

$$(S_x - iS_y)\psi, \quad (S_x - iS_y)^2\psi, \ldots, \quad (S_x - iS_y)^{2S'}\psi$$

represent states degenerate with ψ and of the same total spin S' but with successively lower values of S'_z equal to

$$S'-1, \quad S'-2, \ldots, \quad -S'.$$

Any eigenstate with $S'_z < S'$ may be derived in this way and it will emerge that the state $(S_x - iS_y)^l\psi$ may be regarded as formed from ψ by exciting l spin waves of zero wave vector.

In a state with $S'_z = \frac{1}{2}n$ the α spin sub-band is full and the β spin sub-band contains n holes. If the interaction between electrons were neglected such a state would be represented by a single Slater determinant. It is assumed that when the interaction is present the eigenfunctions of the system with $S'_z = \frac{1}{2}n$ could be derived from single determinants by the methods of many body perturbation theory (Hugenholtz 1957). Any state derivable in this way and thus having a correspondence with a determinantal function of the unperturbed system will be called a 'band-type' state. Band-type states are those normally considered in collective electron theory and correspond to the states with 'no spin waves excited' discussed in H.K. Luttinger (1960) has shown that if the perturbation series converge the concept of a Fermi surface is meaningful and Herring (1960) has considered the evidence for this being so in the transition metals. This generalized band picture is certainly believed to be true for nickel. Thus in particular the low-lying states with $S'_z = \frac{1}{2}n$ may be pictured as having a full α spin band and a partially full β spin band with a few electrons just outside the Fermi surface and a few holes just within it. There are states of all possible total wave vectors with energies infinitesimally above the ground state energy.

2·1. *States with* $S'_z = \frac{1}{2}n-1$

States with one reversed spin are of three distinct types: (*a*) states with total spin $\frac{1}{2}n$ which are derived from states with $S'_z = \frac{1}{2}n$ by applying the operator $S_x - iS_y$; (*b*) band-type states with total spin $\frac{1}{2}n-1$ in which the additional electron in the β spin band occupies a Bloch state outside the Fermi surface and moves quite independently of the hole left in the α spin band; (*c*) states with total spin $\frac{1}{2}n-1$ in which an electron in the β spin band and the hole in the α spin band are bound together in the exciton-like state characteristic of a spin wave. These different types of states will now be discussed qualitatively using an approximation equivalent to that of H (*b*). A more exact discussion of states of type (*c*) is given in § 3.

A state with $S'_z = \frac{1}{2}n$ may be represented approximately by a Slater determinant of total wave vector $\mathbf{p}$

$$\psi_\lambda^{(\mathbf{p})} = [(2N-n)!]^{-\frac{1}{2}}\Delta\{\mathbf{k}_{1\alpha}, \ldots, \mathbf{k}_{N\alpha}; \mathbf{k}_{1\beta}, \ldots, \mathbf{k}_{N-n,\beta}\} \qquad (1)$$

which contains the one-electron functions $b(\mathbf{k}_{i\alpha}, \mathbf{r}_j)\,\alpha(j)$ and $b(\mathbf{k}_{i\beta}, \mathbf{r}_j)\,\beta(j)$. Defining a Wannier function $a(\mathbf{r}-\mathbf{R})$ by

$$a(\mathbf{r}-\mathbf{R}) = N^{-\frac{1}{2}} \sum \exp(-i\mathbf{k}_l.\mathbf{R})\, b(\mathbf{k}_l, \mathbf{r}), \tag{2}$$

where the summation is over all wave vectors, $\mathbf{k}_l$, we can write (1) as

$$\psi_\lambda^{(\mathbf{p})} = [(2N-n)!]^{-\frac{1}{2}} \Delta\{\mathbf{R}_{1\alpha}, \ldots, \mathbf{R}_{N\alpha}; \mathbf{k}_{1\beta}, \ldots, \mathbf{k}_{N-n,\beta}\} \tag{3}$$

which is a determinant containing functions $a(\mathbf{r}_j-\mathbf{R}_i)\,\alpha(j)$ and $b(\mathbf{k}_{i\beta}, \mathbf{r}_j)\,\beta(j)$. Approximate wave functions for states with $S_z' = \frac{1}{2}n-1$ and total wave vector $\mathbf{p}+\mathbf{K}$ may be formed as linear combinations of determinants $\theta_\lambda^{(\mathbf{p})}(\mathbf{k}-\mathbf{K}, \mathbf{k})$ obtained from (1) by replacing $b(\mathbf{k}-\mathbf{K}, \mathbf{r}_j)\,\alpha(j)$ by $b(\mathbf{k}, \mathbf{r}_j)\,\beta(j)$ where the latter state is unoccupied in (1). It follows from H (b) and from § 4 of this paper that within this approximation stationary states exist with wave functions of the form

$$n^{-\frac{1}{2}} \sum_t^{(\bar{\lambda})} \theta_\lambda^{(\mathbf{p})}(\mathbf{k}_l-\mathbf{K}, \mathbf{k}_l) + O(K) \tag{4}$$

for small K where $\Sigma^{(\bar{\lambda})}$ denotes summation over $\mathbf{k}$-vectors of states unoccupied in (1). The states (4) with $K \neq 0$ approximate to states of total spin $\frac{1}{2}n-1$ and in fact to states of type (c); their spin-wave character is easily seen if (4) is rewritten as

$$N^{-\frac{1}{2}} \sum_s \exp(i\mathbf{K}.\mathbf{R}_s)\, \Delta_s, \tag{5}$$

where Δ_s is the determinant obtained from (3) by replacing the function

$$a(\mathbf{r}_j-\mathbf{R}_s)\,\alpha(j) \quad \text{by} \quad c(\mathbf{r}_j-\mathbf{R}_s)\,\beta(j),$$

$c(\mathbf{r})$ being a localized function defined by

$$c(\mathbf{r}) = n^{-\frac{1}{2}} \sum_t^{(\bar{\lambda})} b(\mathbf{k}_l, \mathbf{r}) + O(K).$$

It is straightforward to show the equivalence of (4) and (5), and (5) is clearly a generalization of a Bloch spin wave.

A spin wave in a single band model of a metal may thus be pictured as follows. Consider first a state of maximum spin alinement in which the β spin electrons partially fill a band of Bloch functions, and the α spin electrons may be described either as completely filling such a band or as filling a set of Wannier functions, one on each atom. The determinant Δ_s appearing in (5) is now obtained by removing an α spin electron from the Wannier function at the sth lattice site, reversing its spin, and placing it in a 'partial' Wannier function $c(\mathbf{r}-\mathbf{R}_s)$ localized about the same lattice site. This partial Wannier function is formed only from otherwise unoccupied Bloch functions and is less localized than the Wannier function $a(\mathbf{r}-\mathbf{R}_s)$. The wave function (5) thus represents a situation in which the β spin electron and α spin hole move together through the crystal like an exciton with wave vector K. Except perhaps for terms of order $1/n$ (see the appendix) the energy of this spin-wave state is of the form $E_\lambda + CK^2 + O(K^3)$ for a given direction of $\mathbf{K}$ where E_λ is the energy of the state $\psi_\lambda^{(\mathbf{p})}$ from which the spin-wave state was derived. C is a constant which, for cubic crystals, is independent of the direction of $\mathbf{K}$ and which is effectively the

same for all low-lying initial states $\psi_\lambda^{(p)}$. It is clear from (4) that the wave functions of spin-wave states contain almost equal contributions from many Slater determinants and this property persists in the more exact description of these states given in § 3. Thus a spin-wave state does not have a direct correspondence with a single determinantal function of the interaction-free system and is therefore quite distinct from a band-type state. In the appendix it is shown that spin-wave states may be derived from any low-lying band-type state and that states derived from different band-type states are independent of each other. It should be noted that there are spin-wave states with energies infinitesimally above the ground state.

When $K = 0$ the states (4) reduce to $(S_x - iS_y)\,\psi_\lambda^{(p)}$, apart from a normalizing factor, and are thus states of type (a). States of type (a) are therefore states having a spin wave of zero wave vector excited.

A state of type (b) is a band-type state whose exact wave function has evolved from a single determinant. Even in the case of weak electronic interaction the exact wave function must deviate significantly from a single determinant in order that the hole in the α spin band be screened by electrons of β spin. However, the states of type (b) with low energy may be pictured as obtained from the ground state by removing an electron of wave vector $\mathbf{k}$ at the top of the α spin band and placing it in a state $\mathbf{k}'$ just outside the Fermi surface in the β spin band. Such a state must have an energy of the form

$$E_0 + \epsilon_\beta(\mathbf{k}') - \epsilon_\alpha(\mathbf{k}) + J, \tag{6}$$

where E_0 is the ground-state energy, $\epsilon_\beta(\mathbf{k}')$ and $\epsilon_\alpha(\mathbf{k})$ are quasi-particle energies in the β and α spin bands and J is a positive quantity, containing exchange and correlation energies, which to a first approximation may be assumed independent of $\mathbf{k}$ and $\mathbf{k}'$.

This last assumption may be justified as follows. Suppose, first, that correlation effects are neglected, so that the ground state and the excited state are represented by single determinants; then J may be evaluated simply and, in the limiting case of tightly bound electrons, is independent of $\mathbf{k}$ and $\mathbf{k}'$. The main contribution to J from correlation effects arises from the screening of the α spin hole and this should be independent of $\mathbf{k}'$ and not too dependent on $\mathbf{k}$. Any dependence on $\mathbf{k}$ and $\mathbf{k}'$ individually can be included in the quasi-particle energies.

It follows from (6) that all band-type states with $S_z' = \frac{1}{2}n - 1$ have energies which lie above the ground state energy by a finite quantity which is not less than $J - M$ where M is the maximum value of $|\epsilon_\alpha(\mathbf{k}) - \epsilon_\beta(\mathbf{k}')|$. It is necessary that $J - M$ be positive for the ferromagnetic state to be stable. A second condition for this stability is that spin-wave excitation energies are positive, that is $C > 0$.

2·2. *Statistical mechanics of the system*

So far only states with one spin reversed have been considered and to discuss the thermodynamics of the system a generalization must be made to the case of several spin reversals. It is reasonable to assume that for a small number of spin reversals the excitation energies are additive and the energy of a typical low-lying state of the system, derived from a band-type state by exciting several spin waves, may

then be written down. If the original band-type state has a number of holes in the α spin band and a number of electrons outside and holes inside the Fermi surface in the β spin band, the energy of the state with spin waves excited may be written in the form

$$E_0 - \sum_i p_{i\alpha}[\epsilon_\alpha(\mathbf{k}_i) - \tfrac{1}{2}J] + \sum_{i>f} n_{i\beta}[\epsilon_\beta(\mathbf{k}_i) + \tfrac{1}{2}J] - \sum_{j<f} p_{j\beta}[\epsilon_\beta(\mathbf{k}_j) + \tfrac{1}{2}J] + C\sum_i N_i K_i^2. \quad (7)$$

$p_{i\alpha}$ and $p_{j\beta}$ are occupation numbers for hole states and $n_{i\beta}$, N_i are occupation numbers for electron states and spin-wave excitations, respectively. The summations $i > f, j < f$ are to be carried out over states, respectively, outside and inside the Fermi surface in the β spin band. The first four terms of (7) give the energies of states considered in collective electron theory where the parameter $k\theta'$ occurring in that theory is equal to $\frac{1}{2}J$. The last term of (7) is the excitation energy of several spin waves and the occupation numbers N_i are independent of the occupation numbers in the first four terms. Thus the partition function obtained by summing over all states (7) is the product of two factors, one arising from the states of collective electron theory and one from spin-wave excitations. It follows that the temperature dependence of both the low-temperature specific heat and magnetization may be written as the sum of two terms, one typical of collective electron theory and one of spin-wave theory. Wohlfarth & Cornwell (1960) have attempted to analyze the data of Foner & Thompson (1959) on the temperature variation of the magnetization of nickel by combining terms of the collective electron and spin-wave types. However, they introduce weighting factors α and $1-\alpha$ which does not seem to be justified. A discussion of some experimental results on nickel and nickel–copper alloys is reserved for a later publication.

The qualitative arguments of this section cannot be regarded as rigorous, but it is believed they are essentially correct. They have been given in some detail since the problems considered have hardly been discussed in the literature since the work of Herring & Kittel nearly 10 years ago. It is hoped that the present work may pave the way for more complete discussions.

3. The existence of spin waves and calculation of their energies

The work of Herring & Kittel on the existence of spin waves in metals was summarized in § 1. It was pointed out that their discussions depend, in the case of H.K. on the assumption of a macroscopic exchange energy, or in the case of H (*b*) on a determinantal approximation such as has been used in § 2. Since doubts have been expressed (Van Kranendonk & Van Vleck 1958) as to the existence in metals of spin waves with a well-defined wavelength, a more rigorous proof that such states exist seems desirable. The object of this section is to supply this and to outline a method of calculating spin-wave energies. The only serious assumption made is that a certain perturbation series converges. It should be mentioned that very direct experimental proof of the existence of spin waves in ferromagnetic metals and alloys is provided by the inelastic neutron-scattering experiments of Lowde (1956) and Sinclair & Broekhouse (1960), and by recent spin-wave resonance work (Tannenwald 1961).

Consider a model of n electrons in a band containing N states of each spin, where $n < N$. Thus in the state of maximum spin alinement in the z direction there are n electrons in the α spin band and the β spin band is empty. This model is more convenient to deal with than that of § 2 and the results may be immediately applied to the previous model by interchanging the roles of electrons and holes. The Hamiltonian for the system is

$$H = \sum_i H_i + \tfrac{1}{2}\sum_{i \neq j}\sum v_{ij} + \text{constant},$$

where H_i is the sum of the kinetic energy of the ith electron and its potential energy in the field of the ions and $v_{ij} = e^2/|\mathbf{r}_i - \mathbf{r}_j|$, the coulomb interaction between the ith and jth electrons. One-electron wave functions $b(\mathbf{k}, \mathbf{r})$ and energies $w(\mathbf{k})$ are defined by the equation

$$H_i b(\mathbf{k}, \mathbf{r}_i) = w(\mathbf{k})\, b(\mathbf{k}, \mathbf{r}_i). \tag{8}$$

Suppose the ferromagnetic ground state of the system is non-degenerate with energy $\mathscr{E}$ and has zero total wave vector. It is required to show that spin-wave states with one reversed spin and wave vector $\mathbf{K}$ exist with energies of the form

$$\mathscr{E} + CK^2 + O(K^3), \tag{9}$$

and the proof involves, formally, an actual calculation of these energies. At one point it seems necessary to assume that the crystal has a centre of inversion although one might have expected that the use of time-reversal symmetry would be sufficient.

The starting-point is the ground-state wave function Ψ, corresponding to $S'_z = \frac{1}{2}n$, which is assumed known. In a practical calculation one could normally only find approximations to Ψ but the spin-wave energies should not depend too critically on its exact form. Suppose

$$\Psi = \sum_\lambda a_\lambda \psi_\lambda, \tag{10}$$

where the functions ψ_λ are determinants formed from the one-electron wave functions $b(\mathbf{k}, \mathbf{r}_i)\,\alpha(i)$. Thus one may write

$$\psi_\lambda = \Delta(\mathbf{k}_1, \ldots, \mathbf{k}_n)$$

and

$$\sum_i^{(\lambda)} \mathbf{k}_i = \mathbf{L}, \tag{11}$$

where the summation is over the wave vectors appearing in ψ_λ and $\mathbf{L}$ is a reciprocal lattice vector. The set $\{\psi_\lambda\}$ consists of all determinants satisfying (11) and in the present single-band model the functions of the set must differ from each other by changes of at least two one-electron functions. The ground-state energy is

$$\mathscr{E} = \sum_\lambda |a_\lambda|^2 E_\lambda + \sum_{\lambda \neq \mu}\sum a^*_\lambda a_\mu \langle \psi_\lambda | H | \psi_\mu \rangle, \tag{12}$$

where

$$E_\lambda = \langle \psi_\lambda | H | \psi_\lambda \rangle. \tag{13}$$

The second summation in (12) is over all pairs λ, μ such that ψ_λ and ψ_μ differ by two one-electron functions. Thus suppose

$$\psi_\lambda = \Delta(\mathbf{k}_1, \ldots, \mathbf{k}_i, \ldots, \mathbf{k}_m, \ldots, \mathbf{k}_n)$$

and $$\psi_\mu = \Delta(\mathbf{k}_1, \ldots, \mathbf{k}_{l'}, \ldots, \mathbf{k}_{m'}, \ldots, \mathbf{k}_n),$$

then $$\mathscr{E} = \sum_\lambda |a_\lambda|^2 E_\lambda + \sum_{\lambda \neq \mu} \sum a_\lambda^* a_\mu [\langle lm| v |l'm'\rangle - \langle lm| v |m'l'\rangle], \tag{14}$$

where $$\langle lm| v |l'm'\rangle = \int b^*(\mathbf{k}_l, \mathbf{r}_1)\, b^*(\mathbf{k}_m, \mathbf{r}_2)\, v_{12}\, b(\mathbf{k}_{l'}, \mathbf{r}_1)\, b(\mathbf{k}_{m'}, \mathbf{r}_2)\, \mathrm{d}\tau_{12}.$$

Throughout this section the suffixes l, m, l', m' are used in conjunction with λ, μ to denote the wave vectors of the one-electron functions by which ψ_λ and ψ_μ differ. Another easily obtainable relation is

$$a_\mu^* \mathscr{E} = a_\mu^* E_\mu + \sum_{\lambda \neq \mu} a_\lambda^* [\langle lm| v |l'm'\rangle - \langle lm| v |m'l'\rangle]. \tag{15}$$

By analogy with equation (4) it might be expected that a state derived from Ψ by exciting a spin wave $\mathbf{K}$ would be approximately represented by the wave function

$$\Theta_{\mathbf{K}} = \sum_\lambda a_\lambda \phi_{\lambda \mathbf{K}}, \tag{16}$$

where $$\phi_{\lambda \mathbf{K}} = n^{-\frac{1}{2}} \sum_s^{(\lambda)} \theta_\lambda(\mathbf{k}_s, \mathbf{k}_s + \mathbf{K}). \tag{17}$$

Here $\theta_\lambda(\mathbf{k}_s, \mathbf{k}_s + \mathbf{K})$ is the determinant derived from ψ_λ by replacing the Bloch function $b(\mathbf{k}_s, \mathbf{r}_i)\alpha(i)$ by $b(\mathbf{k}_s + \mathbf{K}, \mathbf{r}_i)\beta(i)$. Certainly $\Theta_0 \propto (S_x - iS_y)\Psi$ and is thus an exact eigenfunction corresponding to a state with a spin wave of zero wave vector excited. It will now be shown that exact eigenfunctions $\Phi_{\mathbf{K}}$ of the system do exist which differ from the $\Theta_{\mathbf{K}}$ only by terms of order K and correspond to energies of the form (9). These eigenfunctions are generalizations of the approximate functions (4) and clearly represent spin-wave states.

An eigenfunction $\Phi_{\mathbf{K}}$ may be formed as a linear combination of $\Theta_{\mathbf{K}}$ and single determinants orthogonalized to $\Theta_{\mathbf{K}}$. A typical determinant which contributes to $\Phi_{\mathbf{K}}$ is

$$\Delta(\mathbf{k}_1, \ldots, \mathbf{k}_{n-1}; \mathbf{q} + \mathbf{K}), \tag{18}$$

where the wave vector $\mathbf{q} + \mathbf{K}$ after the semicolon represents a state of β spin, and

$$\sum_{l=1}^{n-1} \mathbf{k}_l + \mathbf{q} = \mathbf{L}.$$

If the state of spin α and wave vector $\mathbf{q}$ is unoccupied in (18), then the determinant is just $\theta_\lambda(\mathbf{q}, \mathbf{q} + \mathbf{K})$ where θ_λ is derived in the previously described manner from

$$\psi_\lambda = \Delta(\mathbf{k}_1, \ldots, \mathbf{q}, \ldots, \mathbf{k}_{n-1}).$$

However, if the state of spin α and wave vector $\mathbf{q}$ is occupied in (18), then the determinant is not equal to any of the functions θ_λ and new functions must be defined. A typical one is

$$\eta_\nu = \Delta(\mathbf{k}_1, \ldots, \mathbf{k}_l, \ldots, \mathbf{k}_{n-1}; \mathbf{k}_l + \mathbf{K}). \tag{19}$$

These functions are automatically orthogonal to $\Theta_{\mathbf{K}}$ and orthogonalizing $\theta_\lambda(\mathbf{q}, \mathbf{q} + \mathbf{K})$ to $\Theta_{\mathbf{K}}$ the function

$$\chi_\lambda(\mathbf{q}, \mathbf{q} + \mathbf{K}) = \left(1 - \frac{|a_\lambda|^2}{n}\right)^{-\frac{1}{2}} \left\{\theta_\lambda(\mathbf{q}, \mathbf{q} + \mathbf{K}) - \frac{a_\lambda^*}{\sqrt{n}} \Theta_{\mathbf{K}}\right\} \tag{20}$$

is obtained. For the single-band model considered the functions $\Theta_{\mathbf{K}}$, $\chi_\lambda(\mathbf{q}, \mathbf{q}+\mathbf{K})$ and η_ν now form a complete set in which to expand $\Phi_{\mathbf{K}}$. (Strictly one of the functions $\chi_\lambda(\mathbf{q}, \mathbf{q}+\mathbf{K})$ must be omitted to avoid over-completeness.) Expanding $\Phi_{\mathbf{K}}$ in this way, and substituting in the Schrödinger equation

$$H\Phi_{\mathbf{K}} = E(\mathbf{K})\,\Phi_{\mathbf{K}},$$

one is led to a secular equation which may be expanded in the form (Löwdin 1951)

$$E(\mathbf{K}) = \langle\Theta_{\mathbf{K}}|\,H\,|\Theta_{\mathbf{K}}\rangle - \Big\{\sum_\lambda \sum_t{}^{(\lambda)} \frac{|\langle\Theta_{\mathbf{K}}|\,H\,|\chi_\lambda(\mathbf{k}_t, \mathbf{k}_t+\mathbf{K})\rangle|^2}{[\langle\chi_\lambda(\mathbf{k}_t, \mathbf{k}_t+\mathbf{K})|\,H\,|\chi_\lambda(\mathbf{k}_t, \mathbf{k}_t+\mathbf{K})\rangle - E(\mathbf{K})]} + \sum_\nu \frac{|\langle\Theta_{\mathbf{K}}|\,H\,|\eta_\nu\rangle|^2}{\langle\eta_\nu|\,H\,|\eta_\nu\rangle - E(\mathbf{K})}\Big\} + \ldots. \tag{21}$$

It is shown in § 3·1 that for small K the zero-order term of (21) is of the form $\mathscr{E} + C_0 K^2$, that the numerators of higher-order terms are all of order K^2 and that the energy denominators remain finite as $K \to 0$. It follows that if the perturbation series converges, eigenstates exist with energies of the form (9). Further the eigenfunctions $\Phi_{\mathbf{K}}$, for which perturbation series may also be written down, differ from the $\Theta_{\mathbf{K}}$ only by terms of $O(K)$ and thus correspond to spin-wave states. It should be pointed out that all the χ_λ are not exactly mutually orthogonal and this would appear to complicate the higher terms of (21). In fact this complication is not serious as is shown for a special case in § 4.

3·1. *Evaluation of matrix elements*

Using (16) and (17) and the notation

$$\langle l\mathbf{K}, m|\,v\,|l'\mathbf{K}, m'\rangle = \int b^*(\mathbf{k}_l+\mathbf{K}, \mathbf{r}_1)\, b^*(\mathbf{k}_m, \mathbf{r}_2)\, v_{12}\, b(\mathbf{k}_{l'}+\mathbf{K}, \mathbf{r}_1)\, b(\mathbf{k}_{m'}, \mathbf{r}_2)\, \mathrm{d}\tau_{12}$$

one obtains

$$\begin{aligned}\langle\Theta_{\mathbf{K}}|\,H\,|\Theta_{\mathbf{K}}\rangle = \mathscr{E} &+ \sum_\lambda |a_\lambda|^2 [\langle\phi_{\lambda\mathbf{K}}|\,H\,|\phi_{\lambda\mathbf{K}}\rangle - E_\lambda] \\ &+ n^{-1} \sum_{\lambda\neq\mu}\sum a_\lambda^* a_\mu [\langle l\mathbf{K}, m|\,v\,|l'\mathbf{K}, m'\rangle - \langle l\mathbf{K}, m|\,v\,|m'\mathbf{K}, l'\rangle \\ &\quad + \langle l, m\mathbf{K}|\,v\,|l', m'\mathbf{K}\rangle - \langle l, m\mathbf{K}|\,v\,|m', l'\mathbf{K}\rangle \\ &\quad - 2\langle lm|\,v\,|l'm'\rangle + 2\langle lm|\,v\,|m'l'\rangle]\end{aligned} \tag{22}$$

and

$$\begin{aligned}\langle\phi_{\lambda\mathbf{K}}|\,H\,|\phi_{\lambda\mathbf{K}}\rangle - E_\lambda &= n^{-1}\sum_t{}^{(\lambda)} [w(\mathbf{k}_t+\mathbf{K}) - w(\mathbf{k}_t)] \\ &\quad + n^{-1}\sum_s{}^{(\lambda)}\sum_t{}^{(\lambda)} [\langle s\mathbf{K}, t|\,v\,|s\mathbf{K}, t\rangle - \langle st|\,v\,|st\rangle \\ &\quad - \langle t\mathbf{K}, s|\,v\,|s\mathbf{K}, t\rangle + \langle ts|\,v\,|st\rangle].\end{aligned} \tag{23}$$

Evidently, for a given direction of $\mathbf{K}$, (22) is an even function of K if for each $\psi_\lambda = \Delta(\mathbf{k}_1, \ldots, \mathbf{k}_n)$ appearing in (10) with a coefficient a_λ there appears a

$$\psi_{\lambda'} = \Delta(-\mathbf{k}_1, \ldots, -\mathbf{k}_n)$$

with coefficient $\pm a_\lambda$. It is easy to show that this is the case if Ψ is non-degenerate and the crystal has a centre of inversion. Thus in this case the first term in (21) is of the form $\mathscr{E} + C_0 K^2$ for small K.

To evaluate (21) as far as terms in K^2, K may be equated to zero in the energy denominators. The first denominator then becomes

$$\langle\chi_\lambda(\mathbf{k}_t,\mathbf{k}_t)|\,H\,|\chi_\lambda(\mathbf{k}_t,\mathbf{k}_t\rangle-\mathscr{E}=\left(1-\frac{|a_\lambda|^2}{n}\right)^{-1}\{E_\lambda-\mathscr{E}+\sum_{s\neq t}^{(\lambda)}\langle st|\,v\,|ts\rangle\} \tag{24}$$

and a similar expression may be obtained for the second energy denominator. It must now be shown that the matrix elements appearing in the numerators are $O(K)$

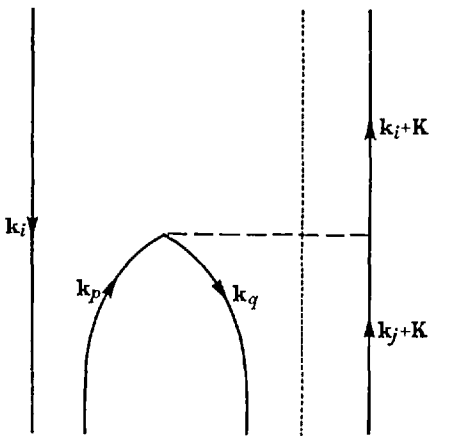

FIGURE 1

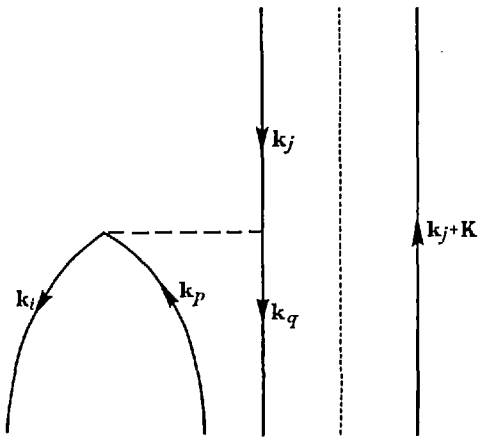

FIGURE 2

and hence that the second-order and higher terms in (21) are $O(K^2)$. From (16), (17), (20) and (15) one obtains

$$\begin{aligned}\langle\Theta_\mathbf{K}|\,H\,|\chi_\lambda(\mathbf{k}_t,\mathbf{k}_t+\mathbf{K})\rangle\,(n-|a_\lambda|^2)^{\frac{1}{2}} = a_\lambda^*\{&w(\mathbf{k}_t+\mathbf{K})-w(\mathbf{k}_t)-[\langle\Theta_\mathbf{K}|\,H\,|\Theta_\mathbf{K}\rangle-\mathscr{E}]\\&+\sum_s^{(\lambda)}[\langle s,t\mathbf{K}|\,v\,|s,t\mathbf{K}\rangle-\langle st|\,v\,|st\rangle\\&-\langle t,s\mathbf{K}|\,v\,|s,t\mathbf{K}\rangle+\langle ts|\,v\,|st\rangle]\}\\&+\sum_{\mu\neq\lambda}a_\mu^*\{\delta_{tl}[\langle m',l'\mathbf{K}|\,v\,|m,l\mathbf{K}\rangle-\langle m'l'|\,v\,|ml\rangle\\&-\langle l',m'\mathbf{K}|\,v\,|m,l\mathbf{K}\rangle+\langle l'm'|\,v\,|ml\rangle]\\&+\delta_{lm}[\langle l',m'\mathbf{K}|\,v\,|l,m\mathbf{K}\rangle-\langle l'm'|\,v\,|lm\rangle\\&-\langle m',l'\mathbf{K}|\,v\,|l,m\mathbf{K}\rangle+\langle m'l'|\,v\,|lm\rangle]\},\end{aligned} \tag{25}$$

which is of order K for small K. The last matrix element to be considered is

$$\langle\Theta_\mathbf{K}|\,H\,|\eta_\nu\rangle=n^{-\frac{1}{2}}\sum_\lambda\sum_s^{(\lambda)}a_\lambda\langle\theta_\lambda(\mathbf{k}_s,\mathbf{k}_s+\mathbf{K})|\,v\,|\eta_\nu\rangle. \tag{26}$$

The interactions of a typical η_ν with functions $\theta_\lambda(\mathbf{k}_s,\mathbf{k}_s+\mathbf{K})$ derived from a particular ψ_λ are represented in the diagrams of figures 1 and 2, which are diagrams of the type used by Goldstone (1957) referred to ψ_λ as vacuum state. Lines representing states of spin α and spin β are drawn to the left and right respectively of the vertical dotted lines. The diagrams correspond to matrix elements

$$\langle\theta_\lambda(\mathbf{k}_s,\mathbf{k}_s+\mathbf{K})|\,v\,|\eta_\nu\rangle \tag{27}$$

with $s = i$ and $s = j$. The only other non-zero matrix element (27) is that with $s = q$ and is represented by figure 1 with i and q interchanged. The sum of these matrix elements gives the contribution to the sum (26) of a particular λ and is of the form

$$\langle q, i\mathbf{K}|\, v\,|p, j\mathbf{K}\rangle - \langle qi|\, v\,|pj\rangle$$
$$-\langle i, q\mathbf{K}|\, v\,|p, j\mathbf{K}\rangle + \langle iq|\, v\,|pj\rangle$$

which is $O(K)$ for small K.

This completes the proof of the existence of spin-wave states and an outline of a general method of calculating spin-wave energies has been given. A further discussion of this general method is given in § 4·2.

4. Spin-wave energies in special cases

4·1. *Herring's approximation*

Existing calculations of spin-wave energies in metals are those of Herring (H (*b*)) and Izuyama (1960). Both these calculations are based on the same approximation and they may be regarded as special cases of the general method presented in § 3. It is of interest to confirm Herring's results using this direct method.

In the notation of § 3, Herring's approximation is equivalent to assuming that the ground state may be represented by a single determinant ψ_0 and that a spin-wave state may be approximated by a linear combination of determinants $\theta_0(\mathbf{k}, \mathbf{k}+\mathbf{K})$. Thus $\mathscr{E} = E_0$, $a_0 = 1$ and $a_\lambda = 0$ for $\lambda \neq 0$. Spin-wave energies may be evaluated within this approximation by omitting all terms involving the functions η_ν in the perturbation series (21) and summing to all orders. The results of § 3 must be slightly modified since the one-electron functions of H (*b*) are not those defined in (8) but solutions of the Hartree–Fock equations. The required modifications are that all matrix elements appearing in (21) must be calculated using the Hartree–Fock one-electron functions and that the one-electron energies $w(\mathbf{k}_i)$ and $w(\mathbf{k}_i+\mathbf{K})$ corresponding to α and β spin states, respectively, must be expressed in terms of Hartree–Fock energies $\lambda_\alpha(\mathbf{k}_i)$, $\lambda_\beta(\mathbf{k}_i+\mathbf{K})$ as follows:

$$\left.\begin{aligned} w(\mathbf{k}_i) &= \lambda_\alpha(\mathbf{k}_i) - \sum_s{}^{(0)}[\langle is|\, v\,|is\rangle - \langle is|\, v\,|si\rangle] \\ w(\mathbf{k}_i+\mathbf{K}) &= \lambda_\beta(\mathbf{k}_i+\mathbf{K}) - \sum_s{}^{(0)}\langle i\mathbf{K}, s|\, v\,|i\mathbf{K}, s\rangle. \end{aligned}\right\} \tag{28}$$

The link between the notation of this paper and that of H (*b*) is that the matrix element $\Phi_{ij}(\mathbf{K})$ of H (*b*) is given by

$$\Phi_{ij}(\mathbf{K}) = \delta_{ij}[\lambda_\beta(\mathbf{k}_i+\mathbf{K}) - \lambda_\alpha(\mathbf{k}_i)] - \langle i\mathbf{K}, j|\, v\,|j\mathbf{K}, i\rangle. \tag{29}$$

As in H (*b*) let
$$\Phi_{ij}(\mathbf{K}) = \Phi^0_{ij} + K\Phi'_{ij} + K^2\Phi''_{ij} + \ldots \tag{30}$$

for a given direction of $\mathbf{K}$; then from (22), (23), (25), (28), (29) and (30) one obtains to $O(K^2)$
$$\langle\Theta_\mathbf{K}|\, H\,|\Theta_\mathbf{K}\rangle - E_0 = n^{-1}K^2\sum_{i,j}\Phi''_{ij}, \tag{31}$$

and to $O(K)$
$$\langle\Theta_\mathbf{K}|\, H\,|\chi(\mathbf{k}_j, \mathbf{k}_j+\mathbf{K})\rangle = (n-1)^{-\frac{1}{2}}K\sum_i\Phi'_{ij}. \tag{32}$$

To evaluate spin-wave energies to $O(K^2)$, K may be equated to zero, not only in the energy denominators, but in all matrix elements between functions $\chi(\mathbf{k}_j, \mathbf{k}_j + \mathbf{K})$ which appear in (21). A typical energy denominator in (21) is given by (24) as

$$\langle\chi(\mathbf{k}_j, \mathbf{k}_j)|\, H\,|\chi(\mathbf{k}_j, \mathbf{k}_j)\rangle - E_0 = (1-1/n)^{-1} \sum_{s\neq j}^{(0)} \langle sj|\, v\,|js\rangle \tag{33}$$

and, remembering that the $\chi(\mathbf{k}_j, \mathbf{k}_j)$ are not mutually orthogonal, a typical non-diagonal element is given by

$$\langle\chi(\mathbf{k}_s, \mathbf{k}_s)|\, H\,|\chi(\mathbf{k}_t, \mathbf{k}_t)\rangle - E_0 \langle\chi(\mathbf{k}_s, \mathbf{k}_s)|\,\chi(\mathbf{k}_t, \mathbf{k}_t)\rangle = -(1-1/n)^{-1}\langle ts|\, v\,|st\rangle. \tag{34}$$

The result of substituting the last four equations into the complete perturbation series (21) is

$$\begin{aligned} E(\mathbf{K}) - E_0 - n^{-1}K^2 \sum_{i,j} \Phi''_{ij} \\ = n^{-1}K^2 \sum_{p=1}^{\infty} \sum_{\mathbf{k}_1 \ldots \mathbf{k}_p}^{(0)} \frac{(\sum_i \Phi'_{i1})\langle 21|\, v\,|12\rangle \ldots \langle p, p-1|\, v\,|p-1, p\rangle\, (\sum_i \Phi'_{pi})}{(\sum_{s\neq 1}^{(0)}\langle s1|\, v\,|1s\rangle) \ldots (\sum_{s\neq p}^{(0)}\langle sp|\, v\,|ps\rangle)}, \end{aligned} \tag{35}$$

where only non-diagonal elements appear in the numerators. Defining a function

$$b_j = b(\mathbf{k}_j) = -\frac{\sum_i \Phi'_{ji}}{\sum_{s\neq j}^{(0)}\langle sj|\, v\,|js\rangle} - \sum_{\mathbf{k}_2} \frac{\langle 2j|\, v\,|j2\rangle\, (\sum_i \Phi'_{2i})}{(\sum_{s\neq j}^{(0)}\langle sj|\, v\,|js\rangle)(\sum_{s\neq 2}^{(0)}\langle s2|\, v\,|2s\rangle)} - \ldots \tag{36}$$

(35) may be written

$$E(\mathbf{K}) - E_0 = n^{-1}K^2\{\sum_{i,j} \Phi''_{ij} + \sum_i (\sum_j \Phi'_{ji})\, b_i\}. \tag{37}$$

Since, from (28), (29) and (30),

$$\Phi^0_{ij} = -\langle ij|\, v\,|ji\rangle + \delta_{ij} \sum_s^{(0)} \langle is|\, v\,|si\rangle,$$

it is easily shown that b_j satisfies the equation

$$\sum_j \Phi^0_{ij} b_j + \sum_j \Phi'_{ij} = 0 \tag{38}$$

which is exactly equation (18) of H (b). The b_j of H (b) thus coincides with that defined by (36), and using (37) and (38) the spin-wave energy is obtained as

$$E(\mathbf{K}) - E_0 = n^{-1}K^2 \sum_{i,j} (\Phi''_{ij} - b^*_j \Phi^0_{ji} b_i),$$

which is just equation (42) of H (b). Using Löwdin's (1951) perturbation formula for the wave function of the spin-wave state equation (44) of H (b) is also easily obtained.

Izuyama (1960) has shown how to calculate spin-wave energies approximately by field theoretical methods for a model which in one respect is more general than that of H (b). His essential approximation (the 'ladder' approximation) is entirely equivalent to that of H (b) but he considers the case in which the ground state is not necessarily the one of complete spin alinement. Izuyama's results are also easily derived by the methods of this section.

4·2. *The possibility of more accurate calculations*

The approximation discussed in § 4·1, in which the ground-state wave function is taken as a single determinant, is obviously only of qualitative value. Strictly this approximation can only be valid for cases in which the electronic interaction energy is negligible compared with the kinetic energy and this situation is incompatible with the existence of ferromagnetism. Now the method described in § 3 allows one, in principle, to go beyond the determinantal approximation. However, the difficulty immediately arises that all the energy denominators in (21) then contain a correlation energy which depends explicitly on the size of the system considered. This difficulty is common in many-body perturbation theory and has been resolved by Hugenholtz (1957). Roth & Pratt (1959), in another connexion, have already applied Hugenholtz's methods in conjunction with Löwdin's form of perturbation series. It is hoped that a similar application to the present problem may make possible more accurate calculations of spin-wave energies.

I am indebted to Dr E. P. Wohlfarth for originally stimulating my interest in the problems discussed in this paper, particularly those of § 2, and for many informative discussions. I am also grateful to him, and to Sir Nevill Mott, F.R.S., for reading the manuscript of this paper and making some helpful suggestions. Thanks are due to the Admiralty for permission to publish this work.

Appendix. Independence of spin-wave states derived from different band-type states

The following discussion is based on the model and the approximation of § 2.

Consider a low-lying band state with $S' = S'_z = \frac{1}{2}n - m$ where $m \ll n$. This state may be pictured as differing from the ground state by having m occupied Bloch states just outside the Fermi surface in the β spin band and m unoccupied Bloch states at the top of the α spin band. The wave function of such a state may be represented approximately by the appropriate Slater determinant ψ_λ. A state derived from this band-type state by exciting a spin wave of wave vector $\mathbf{K}$ has the approximate wave function

$$(n-2m)^{-\frac{1}{2}} \sum_t \theta_\lambda(\mathbf{k}_t - \mathbf{K}, \mathbf{k}_t) + O(K), \tag{39}$$

where the summation is over the wave vectors of Bloch states singly occupied in ψ_λ and an approximate energy of the form $E_\lambda + CK^2$ for small K. Terms in the energy which are linear in K and of order m/n may appear due to the fact that the Bloch states occupied in ψ_λ may not be distributed symmetrically about the origin in $\mathbf{k}$ space, although this is assumed to be the case for the ground state. For states of sufficiently low energy in which $m \ll n$ these linear terms may be neglected.

All low-lying band-type states must have a large number of singly occupied Bloch states in common. It follows that a particular spin-wave state (39) derived from a particular band-type state contains many determinants $\theta_\lambda(\mathbf{k}_t - \mathbf{K}, \mathbf{k}_t)$ which do not contribute to any other spin-wave state. Thus all spin-wave states derived from different band-type states are linearly independent.

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Cubic Field Splitting of D Levels in Metals

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The splitting of the fivefold degeneracy of free atom d electron states by nonspherical components of a crystalline field is calculated. The crystal potential employed is that of a lattice of positive point charges screened by a uniform distribution of electrons. The calculation is done to first order in the cubic field, using hydrogenic electron wave functions. The triply degenerate d state is lowered with respect to the doubly degenerate one in both body-centered and face-centered cubic lattices. Numerical results are given for both lattices. Finally, analytic atomic wave functions are used to estimate the splitting in iron and copper at the observed lattice spacing. The crystal field splitting of these levels is found to be much smaller than the overlap splitting as obtained in previous calculations for both materials.

I. INTRODUCTION

IN a recent calculation, perturbation theory was used to study d bands in the body-centered cubic lattice.[1] The crystal potential employed was that produced by a lattice of point charges of atomic number Z and lattice parameter a, screened by a uniform distribution of valence electrons. The energy of an electron state in this potential can be expressed as (atomic units throughout)

$$E=(Z/a)f(Za)$$

where $f(Za)$ is a function proportional to $(Za)^{-1}$ for small Za. The parameter Za is a measure of the tightness of the binding, and the perturbation calculation reported contained the first three terms in the expansion of the function $f(Za)$ for certain interesting states. The calculation could only be expected to be valid for small Za, but the apparent behavior of the series for large Za led to the conjecture that the d bands in this limit would split into two sub-bands. Within the model considered, such a split could arise only from the departure of the crystal potential around a lattice site from spherical symmetry.

The situation is similar in many respects to that considered in crystal field theory, in which the presence of cubic terms in the crystal potential produces a split of the fivefold degeneracy of the d states of a single electron into a triply degenerate state T_{2g} and a doubly degenerate state E_g.[2] We estimate this splitting for a metal. The calculation, which utilizes the ideas of the tight-binding approximation, considers the potential produced by the lattice of point charges previously mentioned; it can probably be generalized to more complicated situations.

To understand the physical situation in more detail,

[1] J. Callaway, Phys. Rev. 115, 346 (1959). For a review of energy band calculations, see J. Callaway in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7.

[2] A recent review of crystal field theory is given by W. Moffitt and C. J. Ballhausen, Ann. Revs. Phys. Chem. 7, 107 (1956).

consider a hypothetical cubic metal with both s and d electrons, such that the s electrons are distributed reasonably uniformly throughout the atomic cell, but the d electrons are rather tightly bound so that d wave functions on the atomic sites overlap only slightly. The degeneracy of the d levels of the isolated atom would be broken both by the overlaps of the wave functions and by the nonspherical components of the crystal field. For very tightly bound d functions, we would expect the crystal field splitting to be large compared to the overlap splitting. The d levels would then form two sub bands. This is essentially the model which Mott and Stevens[3] have proposed for the body-centered transitions metals. One of the principal reasons for undertaking this calculation was to determine whether the Mott-Stevens model could reasonably be expected to apply to iron. None of the existing energy band calculations for iron supports the Mott-Stevens model[1]; however, all the calculations have neglected crystal field effects.

One of the problems in a tight-binding calculation of energy bands is to determine the expectation value of the crystal potential using atomic wave functions on a single site. This quantity, which is often considered to be the same for all the states in the band, actually contains the crystal field effects in which we are interested. If for simplicity we consider hydrogenic d electron radial wave functions:

$$R_d=(\alpha^7/6!)^{\frac{1}{2}}r^2e^{-\frac{1}{2}\alpha r} \tag{1}$$

the appropriate dimensionless parameter characterizing the physical situation is αa ($\alpha=2Z/3$ for a Coulomb potential). We will later be able to obtain the crystal field splitting for more general wave functions consisting of sums of terms of this form. Large values of αa correspond to small overlap and tight binding. While both the overlap splitting and the cubic field splitting go to zero as $\alpha a\rightarrow\infty$, the overlap splitting goes exponentially while the cubic field depends on $(\alpha a)^{-4}$ as we will show. Thus, for sufficiently large αa the cubic field will dominate.

The problem of crystal field effects in metals has previously been discussed by Leigh.[4] He considered a similar model of the crystal potential, but quite different wave functions. He estimated d band splittings at the observed interatomic spacing only, in iron and copper. The present calculation is of greater generality.

This calculation also contains substantial improvements with respect to conventional crystal field studies which are made possible by the use of a simple model of the crystal potential. We use an expression for the potential which is exact for this model, and do not restrict ourselves to a multipole expansion valid only at distances from the central atom less than the nearest neighbor distance. The use of simple radial functions makes it possible to obtain explicit expressions for all radial integrals, which are conventionally regarded as parameters to be determined from experimental data. Finally, we have evaluated all the pertinent lattice sums.

II. THEORY

The use of a simple lattice model and approximate d electron wave functions permits us to estimate the cubic field effects for a large range of the appropriate parameters. To be precise, we wish to calculate the difference in the energies of the d states of $\Gamma_{25'}$ (xy, yz, zx) symmetry and those of Γ_{12} symmetry (x^2-y^2, $3z^2-r^2$) [5] (t_{2g} and e_g respectively in another notation), of a single electron in a potential field produced by a lattice of positive point charges (atomic number Z) screened by a uniform distribution of electrons so that each cell is electrically neutral. The calculation is the first order in the cubic field only. Spin-orbit coupling is neglected. We define

$$\Delta E=E(\Gamma_{25'})-E(\Gamma_{12})=\int[|\psi(\Gamma_{25'})|^2-|\psi(\Gamma_{12})|^2]V(\mathbf{r})d\tau. \tag{2}$$

ΔE defined by (2) is the negative of the quantity called 10 Dq in the literature of crystal field theory. We put

$$\begin{aligned}\psi(\Gamma_{25'})&=R_d(r)\mathcal{K}_{2,25'}(\theta,\phi),\\ \psi(\Gamma_{12})&=R_d(r)\mathcal{K}_{2,12}(\theta,\phi),\end{aligned} \tag{3}$$

where R_d is given by (1) and $\mathcal{K}_{l,i}$ functions are the appropriate kubic harmonics[6] (order l and representation Γ_i). For example we have

$$\mathcal{K}_{2,25'}=\left(\frac{15}{4\pi}\right)^{\frac{1}{2}}\frac{xy}{r^2};\quad \mathcal{K}_{2,12}=\frac{1}{2}\left(\frac{15}{4\pi}\right)^{\frac{1}{2}}\frac{(x^2-y^2)}{r^2}. \tag{4}$$

Then

$$\Delta E=\int R_d^2(r)[\mathcal{K}^2{}_{2,25'}(\theta,\phi)-\mathcal{K}^2{}_{2,12}(\theta,\phi)]V(\mathbf{r})d\tau. \tag{5}$$

Since $V(\mathbf{r})$ belongs to the completely symmetric (Γ_1) representation of the cubic point group, it follows that if $V(\mathbf{r})$ is expanded in kubic harmonics, the only ones which appear are the $\mathcal{K}_{l,1}$. From the orthonormality properties of the spherical harmonics it follows we need only consider coefficients of $\mathcal{K}_{4,1}$.

$$\mathcal{K}_{4,1}=\frac{5}{4}\left(\frac{21}{4\pi}\right)^{\frac{1}{2}}\left(\frac{x^4+y^4+z^4}{r^4}-\frac{3}{5}\right). \tag{6}$$

[3] N. F. Mott and K. W. H. Stevens, Phil. Mag. 2, 1364 (1957).
[4] R. S. Leigh, Proc. Phys. Soc. (London) 71, 33 (1958).
[5] Notation according to L. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).
[6] F. C. Von der Lage and H. A. Bethe, Phys. Rev. 71, 612 (1947).

We then deduce

$$\Delta E=-\frac{5}{2(21\pi)}\int R_d^2(r)\mathcal{K}_{4,1}(\theta,\phi)V(\mathbf{r})d\tau. \quad (7)$$

We use the Fourier series expression for $V(\mathbf{r})$

$$V(\mathbf{r})=\sum b(\mathbf{K}_n)\exp(i\mathbf{K}_n\cdot\mathbf{r}), \quad (8)$$

where $\mathbf{K}_n$ is a reciprocal lattice vector,

$$\mathbf{K}_n=(2\pi/a)(n_1,n_2,n_3),$$
$$b(\mathbf{K}_n)=-8\pi Z/\Omega_0\mathbf{K}_n^2=-2Za^2/\pi\Omega_0\mathbf{n}^2. \quad (9)$$

Ω_0 is the volume of the unit cell.

In evaluating (7) we make use of the fact that the kubic harmonics are linear combinations of spherical harmonics of order l; for example,

$$\mathcal{K}_{4,1}=(7/12)^{\frac{1}{2}}[Y_{40}+(5/14)^{\frac{1}{2}}(Y_{44}+Y_{4-4})], \quad (10)$$

where the Y_{lm} are normalized spherical harmonics as given, for example, by Bethe and Salpeter.[7] Also, the Fourier transform of a spherical harmonic is proportional to the same spherical harmonic in k space:

$$\int e^{i\mathbf{k}\cdot\mathbf{r}}Y_{lm}(\theta,\phi)d\Omega=4\pi i^l j_l(kr)Y_{lm}(\theta_k,\phi_k) \quad (11)$$

where k, θ_k, ϕ_k are the spherical polar components of $\mathbf{k}$. Thus if we substitute (8) into (7) and perform the integration over solid angle, we obtain

$$\Delta E=-10(\pi/21)^{\frac{1}{2}}\sum b(\mathbf{K}_n)\mathcal{K}_{4,1}(\theta_k,\phi_k)$$
$$\times\int R_d^2(r)j_4(kr)r^2dr. \quad (12)$$

The radial integral can be done for the radial d function given by (1):

$$\int r^6e^{-\alpha r}j_4(kr)dr=\frac{32(5!)\alpha}{k^8(1+\alpha^2/k^2)^6}. \quad (13)$$

If we substitute (13) and (9) into (12), we find after some rearrangement

$$\Delta E=\frac{1280}{3}\frac{\pi Z}{\Omega_0\alpha^4}\left(\frac{\pi}{21}\right)^{\frac{1}{2}}\sum\frac{\mathbf{K}_n^2}{(1+\mathbf{K}_n^2/\alpha^2)^6}\mathcal{K}_{4,1}(\theta_k,\phi_k). \quad (14)$$

Some further simplification is possible using (9) and the explicit representation of the kubic harmonics. The type of lattice (body-centered cubic or face-centered cubic) is involved in (14) through the expression giving the cell volume in terms of the lattice parameter and in the choice of reciprocal lattice vectors $\mathbf{K}_n$. For the body-centered lattice ($\Omega_0=a^3/2$), we have finally

$$\Delta E=\frac{400}{3\pi}\frac{Z}{a}\left(\frac{2\pi}{\alpha a}\right)^4\sum\frac{\mathbf{n}^2}{(1+4\pi^2\mathbf{n}^2/\alpha^2a^2)^6}$$
$$\times\left(\frac{n_1^4+n_2^4+n_3^4}{\mathbf{n}^4}-\frac{3}{5}\right) \quad (15)$$

while for the face-centered lattice, the numerical coefficient is greater by a factor of two. The procedure used here may also be applied to more complicated crystal potentials by suitable choice of the coefficients $b(\mathbf{k}_n)$ in (8).

The series in (5) is not difficult to evaluate for moderate values of αa; however for large αa (say $\alpha a>20$) the convergence of (15) is slow.

For large values of αa, it is necessary to transform the series to a more rapidly convergent form. This can be done in the following manner.

We define the function

$$f(\mathbf{h})=\sum_{\mathbf{K}_n}g(\mathbf{h}-\mathbf{K}_n) \quad (16a)$$

where

$$g(\mathbf{h})=\mathbf{h}^2(1+\mathbf{h}^2/\alpha^2)^{-6}\mathcal{K}_{4,1}(\theta_h,\phi_h). \quad (16b)$$

Then

$$\Delta E=\frac{1280}{3}\left(\frac{\pi}{21}\right)^{\frac{1}{2}}\frac{\pi Z}{\Omega_0\alpha^4}f(0). \quad (17)$$

$f(\mathbf{h})$ is periodic function of $\mathbf{h}$ and thus may be expanded in a Fourier series in the direct lattice.

$$f(\mathbf{h})=\sum_{\mathbf{R}_n}a(\mathbf{R}_n)\exp(-i\mathbf{h}\cdot\mathbf{R}_n). \quad (18)$$

$\mathbf{R}_n$ is a direct lattice vector. The coefficients $a(\mathbf{R}_n)$ are given by

$$a(\mathbf{R}_n)=[\Omega_0/(2\pi)^3]\int f(\mathbf{h})\exp(i\mathbf{h}\cdot\mathbf{R}_n)d\mathbf{h}. \quad (19)$$

With the use of (16), (19) may be expressed as

$$a(\mathbf{R}_n)=[\Omega_0/(2\pi)^3]\int_\infty g(\mathbf{h})\exp(i\mathbf{h}\cdot\mathbf{R}_n)d\mathbf{h}. \quad (20)$$

Then using (11) and (16), we have

$$a(\mathbf{R}_n)=\frac{\Omega_0}{2\pi^2}\mathcal{K}_{4,1}(\theta_R,\phi_R)\int_0^\infty\frac{h^4j_4(hR_n)}{(1+h^2/\alpha^2)^6}dh. \quad (21)$$

With the use of (13), we transform the integral over h to the form

$$\int_0^\infty\frac{h^4j_4(hR)}{(1+h^2/\alpha^2)^6}dh=\frac{\alpha^{11}}{32(5!)}$$
$$\times\int_0^\infty\int_0^\infty r^6e^{-\alpha r}j_4(hr)j_4(hR)dhdr.$$

[7] H. A. Bethe and E. Salpeter in *Handbuch der Physik*, edited by S. Flugge (Springer-Verlag, Berlin, 1957), Vol. 35, p. 91.

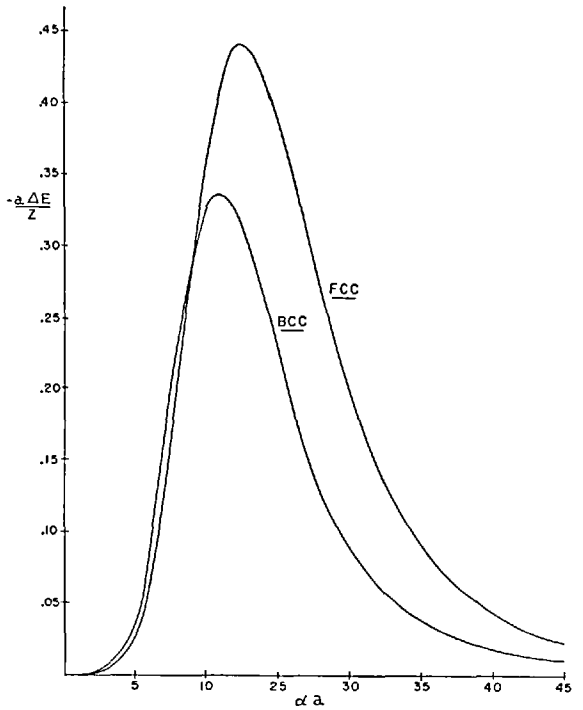

FIG. 1. The cubic field splitting $a\Delta E/Z$ is shown for body-centered cubic and face-centered cubic lattices, based on the numerical data of Table I.

This integral over h can now be done,[8] leaving an elementary integral over r. We obtain

$$\frac{\pi\alpha^{11}}{576(5!)}\left(R^{-5}\int_0^R r^{10}e^{-\alpha r}dr+R^4\int_R^\infty re^{-\alpha r}dr\right)$$
$$=\frac{105\pi}{2R^5}[1-\Phi(\alpha R)];\quad \Phi(x)=e^{-x}\left[\sum_{s=0}^{8}\frac{x^s}{s!}+\frac{9x^9}{10!}\right].$$

But, from (17) and (18)

$$\Delta E=\frac{1280}{3}\left(\frac{\pi}{21}\right)^{\frac{1}{2}}\frac{\pi Z}{\Omega_0\alpha^4}\sum a(\mathbf{R}_n)$$
$$=\frac{11\ 200Z}{a^5\alpha^4}\left(\frac{\pi}{21}\right)^{\frac{1}{2}}\sum\left(\frac{a}{R_N}\right)^5\mathcal{K}_{4,1}(\theta_R,\phi_R)[1-\Phi(\alpha R_N)]$$

where in the last line we have introduced the lattice parameter explicity. Then using (6) for $\mathcal{K}_{4,1}$ we finally have

$$\Delta E=\frac{7000}{(\alpha a)^4}\frac{Z}{a}\sum\left(\frac{a}{R_N}\right)^5[1-\Phi(\alpha R_n)]$$
$$\times(R_{N1}{}^4+R_{N2}{}^4+R_{N3}{}^4-\tfrac{3}{5}\mathbf{R}_N{}^4)/\mathbf{R}_N{}^4. \quad (24)$$

Since $\Phi(\alpha R_n)$ is an exponentially decreasing function, for large αa we may write

$$\Delta E=\frac{7000}{(\alpha a)^4}\frac{Z}{a}\sum\left(\frac{a}{R_N}\right)^5$$
$$\times(R_{N1}{}^4+R_{N2}{}^4+R_{N3}{}^4-\tfrac{3}{5}\mathbf{R}_N{}^4)/\mathbf{R}_N{}^4. \quad (25)$$

Equation (25) may also be obtained more directly by a multipole expansion, as is shown in Appendix 1.

III. RESULTS

It is not necessary to employ sophisticated methods to evaluate the lattice sum in (25) unless great precision is desired. These sums have been carried out approximately for the body-centered and face-centered cubic lattices. The results are -2.131 and -5.163, respectively, with an accuracy of about ± 0.003 in each case. Thus we have

$$\begin{aligned} a\Delta E/Z&=-1.492\times 10^4(\alpha a)^{-4} \text{ for the bcc,}\\ a\Delta E/Z&=-3.614\times 10^4(\alpha a)^{-4} \text{ for the fcc.}\end{aligned} \quad (26)$$

Numerical results for the splitting $a\Delta E/Z$ are presented in Table I and shown graphically in Fig. 1, based on evaluation of (15) and (26). We can conclude that the cubic field splitting tends to lower the energies of functions of the type $\Gamma_{25'}$ with respect of those of Γ_{12} symmetry for all values of the relevant parameters.

A check on the numerical work is provided by the agreement between the values of $a\Delta E/Z$ computed for the bcc lattice for $(\alpha a)^2=12\pi^2$. The sum of the series (15), including 102 different reciprocal lattice vectors is a $aE/Z=-0.0653$. Equation (26) yields for this value of αa; -0.0664. The agreement is already quite good; and inclusion of the function $\Phi(\alpha R_n)$ in the lattice sum using Eq. (24) gave $aE/Z=-0.0653$. A similar agreement between (15) and (24) was found for the fcc lattice at $\alpha a=8\pi$.

It is possible to use these results to make a reasonable estimate of the contribution of the cubic field to the Γ_{25}, Γ_{12} separation in iron at the actual lattice spacing. Of course, d-electron wave functions are more complicated than the simple form (1), but it appears to be possible to express free atom d functions in the form

$$R_d=r^2\textstyle\sum_i N_i e^{-\frac{1}{2}\alpha_i r}. \quad (27)$$

In recent calculations, four terms are included in the sum.[9,10]

ΔE can then be found as a sum of term of the form (15) or (26) provided the change in normalization of the basic functions is properly included. This calculation has been carried out for iron with two different electron wave functions: that found by Lowdin and Appel[9]; and the one determined for the average of all configurations based on d^8 by Watson.[10]

[8] Erdelyi, Magnus, Oberhettinger, and Tricomi, *Tables of Integral Transforms* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. II, p. 47.

[9] P. O. Lowdin and K. Appel, Phys. Rev. 103, 1746 (1956).

[10] R. E. Watson, Technical Report 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (June 15, 1959) (unpublished).

TABLE I. The cubic field splitting a $\Delta E/Z$ is given for body-centered cubic and face-centered cubic latties as a function of αa. The evaluation is based on Eqs. (15) and (24) of the text. For values of αa greater than those given in the table, the simple formula of Eq. (26) will generally suffice.

$(\alpha a/2\pi)^2$	αa	$a\Delta E/Z$ (bcc)	$a\Delta E/Z$ (fcc)
0.0	0.000	−0.00000	−0.0000
0.5	4.443	−0.02351	−0.01245
1.0	6.283	−0.1187	−0.08174
1.5	7.695	−0.2228	−0.1867
2.0	8.886	−0.2938	−0.2873
3.0	10.883	−0.3344	−0.4110
4.0	12.566	−0.3034	−0.4391
5.0	14.050	−0.2538	−0.4146
6.0	15.391	−0.2063	−0.3695
8.0	17.771	−0.1353	−0.2748
10.0	19.869	−0.0918	−0.2011
12.0	21.766	−0.0653	−0.1493
16.0	25.133	−0.0373	−0.0886

We find $E=-0.094Z$ (ev) using the Lowdin function and $E=-0.128Z$ (ev) using the Watson function. The number of free electrons is contained as a parameter in the results, but it is probably reasonable to take $Z=1$. The difference of the results given is of significance only insofar as it indicates the sensitivity of the calculated splitting to the compactness of the wave functions. We can conclude that the cubic field splitting is of the order of $-0.1Z$ ev at the observed interatomic spacing. This would appear to be considerably smaller than the d bandwidth,[1] for any reasonable value of Z, and is in essential agreement with the result of Leigh, obtained in a cruder calculation.[4] These considerations do not support application of the Mott-Steven d-band model applied to iron.

We have also estimated ΔE for copper by the same procedure, using an analytic wave function for Cu^+ from Lowdin and Appel. The result is a cubic field splitting $-0.03Z$ ev at the observed interatomic spacing. The splitting is smaller than in iron because of the greater compactness of the Cu^+ wave functions.

APPENDIX

We give here a derivation of Eq. (25) based on the conventional multipole expansion of the crystal potential. This furnishes a check on the algebra involved in the derivation of that equation. The expansion can be obtained without difficulty, following the work of DeWette and Nijboer.[11] We note first that in the crystal model considered here the uniform distribution of negative charge can contribute only to the spherically symmetric part of the potential, so that we may consider only the point charges. Let these be located at lattice vectors $\mathbf{R}_\lambda$. Then

$$V(\mathbf{r})=-2Z\sum_\lambda|\mathbf{r}-\mathbf{R}_\lambda|^{-1} \qquad \text{(A-1)}$$

(except for the contribution from the negative charge).

We use the expansion

$$|r-R_\lambda|^{-1}=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}\frac{r^l}{R_\lambda^{l+1}}\times Y_{lm}^*(\theta,\phi)Y_{lm}(\theta_R,\phi_R) \qquad \text{(A-2)}$$

which is valid for r smaller than the nearest neighbor distance. We are only interested in the part of the expansion involving $l=4$, which we call V_4. The lattice constant a is also introduced;

$$V_4=-\frac{2Z}{a}\left(\frac{4\pi}{9}\right)\frac{r^4}{a^4}\sum_m\left[Y_{4m}^*(\theta,\phi)\sum_{R_\lambda}\left(\frac{a}{R_\lambda}\right)^5\times Y_{4m}(\theta_R,\phi_R)\right]. \qquad \text{(A-3)}$$

On account of the symmetry of the crystal, the sums in (20) must produce the kubic harmonic $\mathcal{K}_{4,1}$. It is found that

$$V_4=-\frac{2Z}{a}\left(\frac{r}{a}\right)^4\mathcal{K}_{4,1}(\theta,\phi)B \qquad \text{(A-4)}$$

where B is a numerical coefficient

$$B=\frac{4\pi}{9}\left(\frac{12}{7}\right)^{\frac{1}{2}}\sum_{R_\lambda}Y_{40}(\theta_R,\phi_R)\left(\frac{a}{R_\lambda}\right)^5. \qquad \text{(A-5)}$$

With the use of (A-4), the explicit representation of the radial function, and the orthonormality of the kubic harmonics, ΔE, as given by Eq. (7) may be evaluated:

$$\Delta E=\frac{2.52\times10^4}{(21\pi)^{\frac{1}{2}}}\frac{BZ}{a(\alpha a)^4}. \qquad \text{(A-6)}$$

We must now evaluate B. Since the atoms are in "cubic" positions, the sum of Y_{40} over all the atoms of a given type [say those located at $R_\lambda=a(3,2,1)$] is proportional to the kubic harmonic $\mathcal{K}_{4,1}$. We find that

$$B=\frac{5}{18}(21\pi)^{\frac{1}{2}}\sum_{R_\lambda}\left(\frac{a}{R_\lambda}\right)^5\times(R_1^4+R_2^4+R_3^4-\tfrac{3}{5}\mathbf{R}_\lambda^4)/\mathbf{R}_\lambda^4. \qquad \text{(A-7)}$$

Equation (23) is substituted in (A-6) to obtain

$$\Delta E=\frac{7000}{(\alpha a)^4}\frac{Z}{a}\sum_{R_\lambda}\left(\frac{a}{R_\lambda}\right)^5\times(R_1^4+R_2^4+R_3^4-\tfrac{3}{5}\mathbf{R}_\lambda^4)/\mathbf{R}_\lambda^4. \qquad \text{(A-8)}$$

Equation (A-8) agrees exactly with (25) of the text.

If we replace Eq. (A-2) by the complete multipole expansion which has radial dependence R_λ^l/r^{l+1} for $r>R_\lambda$, we obtain, by a similar procedure, Eq. (24). This result demonstrates the complete equivalence of the procedures based on the Fourier series and on the multipole expansion of the crystal potential.

[11] F. W. DeWette and B. R. A. Nijboer, Physica 24, 1105 (1958).