

CONDUCTION ELECTRONS IN A MAGNETIC FIELD

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## ABSTRACT

In this paper, three problems that involve the behavior of conduction electrons in a magnetic field are considered: the change of resistance in a magnetic field, the setting up of a tightly bound electron approximation in a magnetic field, and the effect of a magnetic field on Floquet's theorem.

To treat the change of resistance of monovalent metals in a magnetic field, we use the nearly free electron approximation. Analytical methods for the evaluation of the integrals that arise in the usual treatment are developed by expressing the energy and relaxation time in terms of series of cubically symmetrical spherical harmonics. Numerical results of the correct order of magnitude can be obtained for the Hall coefficient and the coefficients of the change of resistance. However, contrary to the available observations, the ratio of the transverse to the longitudinal change of resistance has a minimum value of about four. The breakdown of Ohm's law at high current densities is considered and a qualitative, physical discussion of the various phenomena is given.

In an attempt to get wave functions that satisfy Schrödinger's equation when the magnetic field is included in the Hamiltonian, we consider the extension of the tightly bound electron approximation in which the atomic wave functions are those for atoms in a magnetic field. The problem is set up, the necessary integrals are evaluated, and the

problem is reduced to the solution of a set of simultaneous equations. Various methods of solution are considered in detail, but the general case proves to be intractable. When considering boundary conditions, we find that in order to have cyclic boundary conditions the magnetic field must be limited to a constant that is inversely proportional to the square of the period of the cycle. Some indication of the properties of a general crystal is obtained by determining the energy levels and the magnetic susceptibility of a two by two square lattice.

A theorem fundamental to much of the electron theory of metals is Floquet's theorem, which states that the wave functions of an electron in a crystal lattice can always be chosen so that they have the form  $\psi(\underline{r}) = \exp(i\underline{k} \cdot \underline{r})u(\underline{r})$  where  $u(\underline{r})$  has the periodicity of the lattice. We find that the usual proof of this theorem breaks down in a magnetic field and it appears that the ordinary form of the theorem does not hold there. It would also seem that the important method invented by Wigner and Seitz, and extended by Slater, for the treatment of cohesion is not valid in a magnetic field.

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PREFACE

In this paper three problems are considered. While no attempt is made to give a systematic treatment of the entire question of the effect of a magnetic field on the conduction electrons, by the time we have considered the three problems and some of the related topics that they suggest, we will have a fairly complete survey of this question.

The two general methods of treating the conduction electrons in a metal are by the use of the nearly free electron approximation and by the use of the tightly bound electron approximation. Neither approximation gives a very good description of the state of the conduction electrons, since this state lies in the intermediate region where neither approximation is really valid. If any problem can be treated by both approximations, the common features are usually accepted as giving a true description of the state. Frequently only one approximation is useful and then one can only regard the results as giving an indication of the actual state of a metal.

We will use the nearly free electron approximation to discuss the Hall effect and the change of resistance in a magnetic field. Here we assume that the electronic states are the plane waves of free electrons, modified by the periodic lattice potential. The effect of electric and magnetic fields is given by a continuous change of the electrons from state to state. Interactions with the lattice cause the electrons to

tend toward a state of thermal equilibrium with the lattice. The balance between these two oppositely directed tendencies is expressed mathematically by means of Boltzmann's equation and the use of a relaxation time. This treatment is particularly adapted to transport problems so that we will use it to treat the Hall effect and the increase in electrical resistance produced by a magnetic field. When considering the use of a relaxation time, it will be pertinent to consider its use in treating the deviations from Ohm's law at high current densities although no magnetic field is involved.

We ought to be able to determine the effect of a magnetic field on the conduction electrons more accurately if we use wave functions that are solutions of Schrödinger's equation when a magnetic field is present than if we think of the magnetic field as a perturbation that shifts the electron from one state to another where these states are represented by wave functions that are exact only when there is no magnetic field. The tightly bound electron approximation seems to be the appropriate one to use in finding wave functions that are valid in a magnetic field since all that we will have to do is use a linear combination of atomic functions that include the effect of the field. We examine in considerable detail the question of boundary conditions, and, in particular, that of cyclic boundary conditions. The most useful and most accurate information given by this treatment is the energies of the states, and from this we can calculate the magnetic

susceptibility. In the general case the problem can be reduced to the solution of a difference equation or the reduction to diagonal form of a matrix. This is carried out for a two by two lattice and the susceptibility of such a crystal, or molecule, is determined.

When there is no magnetic field, Floquet's theorem states that the wave functions of an electron in a crystal lattice can always be chosen so that they are of the form  $\psi(\underline{r}) = \exp[i\underline{k} \cdot \underline{r}] u_{\underline{k}}(\underline{r})$  where  $u_{\underline{k}}(\underline{r})$  has the periodicity of the lattice. This theorem is of fundamental importance throughout the theory of metals and we would like to use it in the closely bound electron approximation. However, investigation shows that the usual proof of the theorem breaks down in a magnetic field and there are indications that if there is any analogue of the theorem that holds in a magnetic field, its form is considerably different from the usual form. While investigating the widespread consequences that will follow if no analogue of Floquet's theorem can be found that holds in a magnetic field, we consider the effect of a magnetic field on the important method invented by Wigner and Seitz, and extended by Slater, for the investigation of cohesion. We find that apparently these methods cannot be used in a magnetic field.

In making this survey of the behavior of conduction electrons in a magnetic field by considering the change of

resistance in a magnetic field, the setting up of a tightly bound electron approximation in a magnetic field, and the effect of a magnetic field on Floquet's theorem, it will be assumed that the usual electron theory of metals as given in any of the standard works on the subject is well known and need not be repeated.

To Professor W. V. Houston I wish to express my deep gratitude for his continued interest in the research on which this paper is based and for his very helpful advice at all stages of the work.



# CHANGE OF RESISTANCE IN A MAGNETIC FIELD

## §1. Introduction

Change of resistance in a magnetic field cannot be interpreted in terms of a free electron picture. But since such a change is observed in the alkalis, it is of interest to see if it can be understood as a small departure from the free electron situation. Jones and Zener [9]\* have given a theory for this effect that seems to give quite satisfactory numerical results in the case of lithium. However, their approximate method of evaluating the integrals made it necessary to apply, later, an estimated correction factor of about six. This paper attempts to give a method of evaluating these integrals, and the corresponding integrals that occur in the general theory of the Hall effect, that will enable one to get analytically as good an approximation as is desired, provided the surfaces of constant energy are not too irregular. Also it is not assumed that the relaxation time is a function of the energy only. §2 gives a summary of the general theory, in Wilson's [18] notation, and §3 gives a physical picture of the situation, in which particular attention is given to the free electron case. In §4 the energy and the relaxation time are expressed in terms of series of cubically symmetric spherical harmonics. By a proper choice of independent

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\*Such numbers in square brackets refer to the bibliography.

variables, the integrals can all be evaluated in terms of the coefficients of the spherical harmonics. If the first two terms of the series are taken as a satisfactory approximation, expressions are obtained for the conductivity, the Hall coefficient, and the two coefficients,  $B_t$  and  $B_\lambda$ , of the change of resistance in a magnetic field. In §5 the conclusions that may be drawn from these expressions are discussed. It is found that theory and experiment give radically different values of  $B_t/B_\lambda$ . Experimentally this ratio is about unity, while no choice of parameters can give a theoretical value less than 4. The expressions for  $B_t$  and  $B_\lambda$  show that the variation of the relaxation time with direction, as well as with energy, is nearly as important in all these effects as the fact that the surfaces of constant energy are not spheres. §6 discusses the breakdown of Ohm's law in high electrostatic fields in cases where a relaxation time exists and where it is not necessary to neglect the third power of the relaxation time compared to the first. The result, in the free electron case, is about one thirtieth as large as Guth and Mayerhöfer's [7] and has the opposite sign. This may indicate that the use of high powers of the relaxation time in §§2-6 is not allowable.

## §2. General Results

We will specify the state of an electron in the usual manner by the wave vector  $\underline{k}$  whose Cartesian components

are  $(k_1, k_2, k_3)$ . The energy eigenfunctions of the electrons when unperturbed by external fields can be taken as

$$\psi_{\underline{k}}(\underline{r}) = \exp(i\underline{k} \cdot \underline{r}) u_{\underline{k}}(\underline{r}),$$

where  $u_{\underline{k}}(\underline{r})$  has the periodicity of the lattice. The number of electrons per unit volume whose wave vectors lie in the range  $(dk_1, dk_2, dk_3)$  is

$$(1/4\pi^3) f(\underline{k}) dk_1 dk_2 dk_3.$$

We omit any dependence on  $\underline{r}$  since we are going to be interested only in the case in which the temperature and composition of the metal are independent of  $\underline{r}$ .

If there exist in the metal an electric field,  $\underline{\mathcal{E}}$ , and a magnetic field,  $\underline{H}$ , then the condition that the distribution function,  $f(\underline{k})$ , remains constant in time under the influence of the fields and the collisions of the electrons with the lattice points is given by Boltzmann's equation,

$$- (e/\hbar) [\underline{\mathcal{E}} + \underline{v}_{\underline{k}} \times \underline{H}/c] \cdot \text{grad}_{\underline{k}} f + (f - f_0)/\tau(\underline{k}) = 0, \quad (1)$$

where  $-e$  is the charge of an electron,  $\underline{v}_{\underline{k}}$  is the velocity associated with the state  $\underline{k}$ , and  $f_0$  is the value of  $f$  when  $\underline{\mathcal{E}} = \underline{H} = 0$ . We have assumed that a relaxation time,  $\tau(\underline{k})$ , can be defined so that we can use this form of Boltzmann's equation. A relaxation time can be used if the temperature is greater than the Debye characteristic temperature, and perhaps

under other conditions. Eq. (1) is only valid if  $eH\tau/2mc \ll 1$ , where  $m$  is the mass of the electron and  $c$  is the velocity of light.

To solve Eq. (1), take the direction of the magnetic field as the  $z$  axis and substitute for  $\underline{v}$  its value in terms of  $\underline{k}$ ,

$$\underline{v}_{\underline{k}} = (1/\hbar) \text{grad}_{\underline{k}} E(\underline{k}), \quad (2)$$

where  $E(\underline{k})$  is the energy associated with the state  $\underline{k}$ . Let  $f = f_0 - \Phi(\underline{k}) \partial f_0 / \partial E$ . It follows from (1) that the equation that  $\Phi(\underline{k})$  is to satisfy is

$$\Phi(\underline{k})/\tau(\underline{k}) + (e/\hbar)\underline{\mathcal{E}} \cdot \text{grad}_{\underline{k}} E - (eH/\hbar^2 c)\Omega\Phi(\underline{k}) = 0, \quad (3)$$

where the product of  $\underline{\mathcal{E}}$  and  $\Phi$  is neglected, and  $\Omega$  is the operator

$$\Omega = \frac{\partial E}{\partial k_2} \frac{\partial}{\partial k_1} - \frac{\partial E}{\partial k_1} \frac{\partial}{\partial k_2}.$$

This process is equivalent to a development of  $f$  as a power series in the components of  $\underline{\mathcal{E}}$  and the neglect of all terms of higher than the first degree. The validity of this development is discussed on p. 22.

To solve Eq. (3) we write  $\Phi(\underline{k})$  as a power series in  $H$ , and obtain

$$\begin{aligned} \Phi(\underline{k}) = & - (\epsilon/\hbar) \left\{ \tau \underline{\xi} \cdot \text{grad. } E \right. \\ & + (\epsilon H/\hbar^2 c) \tau \Omega (\tau \underline{\xi} \cdot \text{grad. } E) \\ & \left. + (\epsilon H/\hbar^2 c)^2 \tau \Omega [\tau \Omega (\tau \underline{\xi} \cdot \text{grad. } E)] + \dots \right\}. \end{aligned} \quad (4)$$

This is one particular integral of (3) and may or may not be the solution we desire. The general solution of (3) is obtained by adding to (4) the general solution of

$$\begin{aligned} \Phi_1(\underline{k}) = & \tau(\underline{k}) (\epsilon H/\hbar^2 c) \Omega \Phi_1(\underline{k}) \\ = & (\tau \epsilon H/\hbar^2 c) [\text{grad.}_k \Phi_1(\underline{k})] \cdot [\text{grad.}_k E(\underline{k})] \times \underline{e}_3 \end{aligned}$$

where  $\underline{e}_3$  is a unit vector in the  $k_3$  direction. Consider the curve of intersection of any surface of constant energy with the plane  $k_3 = 0$ . The vector  $(\text{grad.}_k E) \times \underline{e}_3$  will be directed along this curve. In all cases of interest  $E(\underline{k})$  is such that this vector is directed in the clockwise sense of describing the curve. Since  $\tau(\underline{k})$  is essentially positive, our equation shows that the component of  $\text{grad.}_k \Phi_1$  in the direction of  $(\text{grad.}_k E) \times \underline{e}_3$  is always of the same sign as  $\Phi_1$ . Hence if we traverse our curve in the clockwise sense,  $|\Phi_1|$  will increase unless  $\Phi_1 = 0$ . Therefore the only single-valued solution of the homogeneous equation is  $\Phi_1 = 0$ . Hence (4) is the desired solution of (3).

To discuss the convergence of the infinite series (4), we will make the simplest possible assumptions. We will

assume that the energy is that for the free electron case and that the relaxation time is a spherically symmetric function of  $\underline{k}$ . It follows that the condition that the series converge is that  $\epsilon H \tau / mc < 1$ . Since we have already had to require that  $\epsilon H \tau / mc \ll 1$ , we can hope for convergence in those cases in which  $E$  and  $\tau$  do not have these simple forms. We can also expect that only a few terms of the series will be needed to represent  $\phi$  with satisfactory accuracy.

The reason that we can terminate the series in the components of  $\underline{E}$  with the linear terms while we must include at least the quadratic term in the series in  $H$  is that the magnetic force is very much larger than the electrostatic for electrons whose representative points are at the surface of the Fermi distribution. If the current density in silver is 10 amp.  $\text{cm}^{-2}$ , and if the magnetic field is 1000 gauss, the magnetic force is  $10^8$  times as great as the electric force.

We can get expressions for the conductivity, the Hall coefficient, and the change of resistance in a magnetic field by substituting the value of  $\phi$  found above in the equation giving the current density,

$$\begin{aligned} \underline{J} &= - (\epsilon / 4\pi^3) \int \underline{v}_{\underline{k}} f(\underline{k}) dV \\ &= (\epsilon / 4\pi^3 \hbar) \int \text{grad} \cdot \underline{k} E (\partial f_0 / \partial E) \phi dV, \quad (5) \end{aligned}$$

where  $dV$  is an element of volume in  $\underline{k}$ -space.

To do this we introduce the following abbreviations:

$$I_1 = - \int \tau (\partial f_0 / \partial E) (\partial E / \partial k_1)^2 dV,$$

$$I_2 = - \int \tau (\partial f_0 / \partial E) (\partial E / \partial k_2)^2 dV,$$

$$I_3 = - \int \tau (\partial f_0 / \partial E) (\partial E / \partial k_3)^2 dV,$$

$$I_4 = I_2 I_6 - I_7^2,$$

$$\begin{aligned} I_5 &= \int \tau \frac{\partial f_0}{\partial E} \frac{\partial E}{\partial k_3} \Omega \left\{ \tau \Omega \left( \tau \frac{\partial E}{\partial k_3} \right) \right\} dV \\ &= - \int \tau \frac{\partial f_0}{\partial E} \left\{ \Omega \left( \tau \frac{\partial E}{\partial k_3} \right) \right\}^2 dV, \end{aligned} \quad (6)$$

$$\begin{aligned} I_6 &= \int \tau \frac{\partial f_0}{\partial E} \frac{\partial E}{\partial k_1} \Omega \left\{ \tau \Omega \left( \tau \frac{\partial E}{\partial k_1} \right) \right\} dV \\ &= - \int \tau \frac{\partial f_0}{\partial E} \left\{ \Omega \left( \tau \frac{\partial E}{\partial k_1} \right) \right\}^2 dV, \end{aligned}$$

$$\begin{aligned} I_7 &= \int \tau \frac{\partial f_0}{\partial E} \frac{\partial E}{\partial k_1} \Omega \left( \tau \frac{\partial E}{\partial k_2} \right) dV \\ &= - \int \tau \frac{\partial f_0}{\partial E} \frac{\partial E}{\partial k_2} \Omega \left( \tau \frac{\partial E}{\partial k_1} \right) dV. \end{aligned}$$

The second form of each integral is obtained by integrating the first form by parts.

For those metals in which  $E(\underline{k})$  and  $\tau(\underline{k})$  are even functions of  $k_1$ , of  $k_2$ , and of  $k_3$ , we find that if the current flows in the x-direction only, the electrical conductivity in the absence of a magnetic field is

$$1/\rho = \sigma = J_x/E_x = (\epsilon^2/\pi h^2)I_1, \quad (7)$$

the Hall coefficient is

$$R = E_y/HJ_x = E_y/H\sigma E_x = - (4\pi^3/c\epsilon)I_7/I_1I_2, \quad (8)$$

and the coefficients of the change of resistance in magnetic fields that are perpendicular and parallel, respectively, to the direction of the current are

$$B_t = (\rho - \rho_0)/\rho_0 H^2 = (\sigma_0 - \sigma)/\sigma H^2 = (\epsilon/\hbar^2 c)^2 I_4/I_1I_2 \quad (9)$$

and

$$B_{\parallel} = (\rho - \rho_0)/\rho_0 H^2 = (\sigma_0 - \sigma)/\sigma H^2 = (\epsilon/\hbar^2 c)^2 I_5/I_3. \quad (10)$$

By Schwarz's inequality the change of resistance is always an increase. These formulas are equivalent to those given by Wilson [18].

Equations (7)-(10) were derived under the implicit assumption that  $E(\underline{k})$  and  $\tau(\underline{k})$  had cubic symmetry. However, if  $E$  and  $\tau$  are even functions of  $k_1$ , of  $k_2$ , and of  $k_3$ , these



equations still hold provided we replace  $\sigma$  by  $\sigma_x$ , the conductivity in the x-direction, add the equations  $\sigma_y = (e^2/\pi h^2)I_2$  and  $\sigma_z = (e^2/\pi h^2)I_3$ , and replace  $R$  by  $R_x$ , the Hall coefficient when the current is flowing in the x-direction, etc.

### §3. Physical Picture

A careful study of the above equations enables one to get a physical picture of what is going on. In the absence of external forces, the distribution of representative points in  $\underline{k}$ -space is given by the Fermi function,  $f_0(\underline{k})$ . The density of distribution depends on the energy only. The application of a force,  $\underline{F}$ , causes the distribution of representative points to drift in the direction of the force, since <sup>the</sup> rate of change of the state of an electron is given by

$$d\underline{k}/dt = \underline{F}/\hbar.$$

When we assume the Boltzmann equation in the form of Eq. (1), we are really assuming that the effect of the collisions of the electrons with the ions is such that the actual distribution,  $f$ , differs at each point from the normal distribution,  $f_0$ , by an amount that is proportional to the rate at which  $f$  would tend to be changed by the drift produced by the force. We are not assuming that a representative point drifts for a certain time or distance, on the average, before a collision changes its state.

Our series solution of Boltzmann's equation is really a solution by successive approximations. Rather than consider the effect of the drift produced by the external forces on the final unknown distribution, we first calculate the change in distribution on the assumption that only the representative points of the undisturbed function,  $f_0$ , drift. Hence from Eq. (1) we see that in the first approximation we must add to the equilibrium distribution function the term

$$- \tau \underline{F} \cdot \text{grad} \cdot \underline{k} f_0.$$

We get the second approximation by considering the drift of those points given by the first approximation and obtain

$$- \tau \underline{F} \cdot \text{grad} \cdot \underline{k} [-\tau \underline{F} \cdot \text{grad} \cdot \underline{k} f_0].$$

Each additional term is found by considering the action of the forces on the representative points given by the previous term.

Since the forces on conduction electrons due to magnetic fields in metals are, in general, much greater than those due to electric fields, we include the electric forces in the first term only of this series of approximations. We do not include the magnetic forces in this first term since the drift produced by them is perpendicular to  $\underline{v} = \text{grad} \cdot \underline{k} E/h$ . It is, therefore, along the surfaces of constant energy and produces no change in the undisturbed distribution. The

first approximation gives the ordinary conductivity, the second gives the Hall effect, and the third gives the change of resistance in a magnetic field.

Let us consider our picture of the free electron case. We may assume complete degeneracy since Sommerfeld and Frank [15] have shown that the departure from complete degeneracy gives only about one-ten-thousandth of the observed change of resistance in a magnetic field. Therefore when no external field is applied, the density of representative points is uniform inside a certain sphere and zero outside. When an external field is applied, the change in the distribution function is given by a surface density of representative points on this sphere. We show this in Fig. 1 by taking a cross section in  $k$ -space through the plane  $k_3 = 0$ . The circle represents the interaction of the sphere with this plane and the width of the surrounding band indicates the surface density of representative points. Black indicates a positive and white a negative

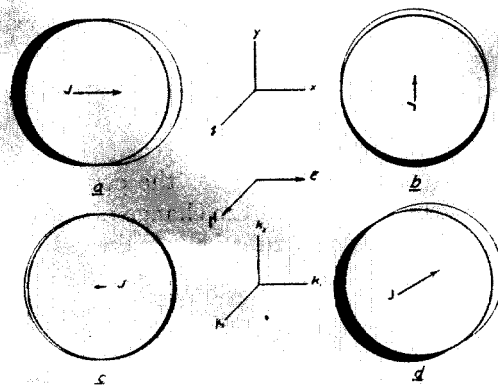


FIG. 1. The free electron case. Since the charge of the electron is taken to be negative, the representative points drift in a direction opposite to that of the electric field.

surface density. For the case in which the electric field is in the x direction and the magnetic field is in the z direction, Fig. 1 (a) shows the effect of the electric field on the undisturbed distribution. Fig. 1 (b) gives the second approximation and shows the effect produced by the action of the magnetic field on the surface density of representative points shown in (a). Fig. 1 (c) gives the third approximation and shows the effect produced by the magnetic field on the points that make up the second approximation. The actual distribution, shown in (d), is obtained by superposing these three terms.

It is evident that if the electric field is in the x direction, then the current is not. But all the effects are defined for the case in which the current is in the same direction, with and without the magnetic field. Hence the Hall effect arises from the fact that to eliminate the current indicated in (b) we will need to apply an electric field in the negative y direction. Fig. 1 (c) would seem to indicate that the current is less when we have a magnetic field, that is, that the magnetic field increases the resistance. But if we consider the Hall effect of the electric field introduced to suppress the y component of the current, we see that if we have spherical symmetry, this effect completely cancels out and there is no change of resistance.

If the magnetic field is parallel to the current, the application of an electric field yields, if we have

spherical symmetry, a first approximation that has cylindrical symmetry about an axis parallel to the magnetic field. Therefore the magnetic field produces no change in the distribution function and hence no change of resistance.

If we do not have spherical symmetry, we must remember that the velocity is in a direction perpendicular to the surfaces of constant energy. The interaction of effects is very complicated, but, by a sufficient extension of this kind of argument, it can be seen in a qualitative way that the effect of all departures from spherical symmetry is a tendency to increase the resistance in a magnetic field. If the departures are small, the Hall effect is not greatly changed.

If the departures from spherical symmetry are large, then by proper choice of the shapes of the surfaces of constant energy it is easy to explain the fact that the Hall coefficient is positive in some metals. For example, Fig. 2 shows how the anomalous Hall effect arises in the case of a cubic Brillouin zone that is so nearly filled that only spherical segments are left unoccupied in the corners. Fig. 2 (a) is a cross section at the surface of the Brillouin zone. The quadrants separate the occupied and unoccupied regions of  $\underline{k}$ -space, and the arrows indicate the velocity in coordinate space of electrons whose representative points are at the indicated positions on the boundary of the distribution. Fig. 2 (b), like Fig. 1 (a), shows the effect of the electric field on the undisturbed distribution. Fig. 2 (c), like

Fig. 1 (b), gives the second approximation and shows the effect produced by the action of the magnetic field on the surface density of representative points shown in Fig. 2 (b). Since the current due to the representative points of the

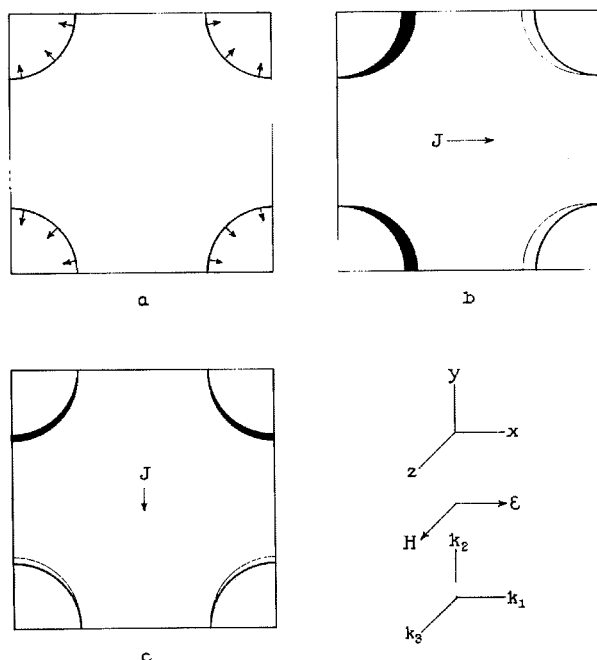


Fig. 2. Anomalous Hall effect

second approximation in Fig. 2 is in the opposite direction to the current due to the representative points of the second approximation in Fig. 1, the coefficient of the Hall effect will have the opposite sign.

#### §4. Calculations

Equations (9) and (10) give us analytical expressions for the change of resistance in a magnetic field in terms of certain integrals. For completely free electrons  $I_4=I_5=0$  if we assume complete degeneracy in evaluating the integrals; hence we get no change of resistance for free electrons. Sommerfeld and Frank [15] showed that if we take account of the departure of the electrons from complete degeneracy, we get a change of resistance but that it is about 10,000 times too small and has the wrong temperature dependence. A first order change of resistance is only obtained if either  $\tau$  is not a function of  $E$  only or the surfaces of constant energy are not spheres. To be consistent one should not treat these conditions as independent since one would expect that whenever the energy surfaces are not spheres,  $\tau$  would depend on the direction of motion. One would also expect that the change of resistance produced by the fact that  $\tau$  does not depend on  $E$  alone would be of the same order of magnitude as that produced by the fact that the surfaces of constant energy are not spheres.

Jones and Zener [9] have evaluated these integrals for the case of lithium by an approximate method that made it necessary to apply, later, an estimated correction factor of about six. Blochinzev and Nordheim [4] considered divalent metals and used a model in which the conduction was due to

both the electrons and the holes. If the energy surfaces in the upper zone were taken to be ellipsoids with axes whose lengths are properly chosen, results of the correct order of magnitude could be obtained. In both papers it was assumed that the relaxation time was a function of the energy only.

We will attempt to develop a method of evaluating these integrals in cases where the surfaces of constant energy are not too irregular that will include the corrections that Jones and Zener had to estimate and that will not require the relaxation time to be a function of the energy only.

In the case of the monovalent metals we expect that the surface of the Fermi distribution will lie entirely within the first Brillouin zone and will be nearly spherical. By expressing the dependent variables in terms of spherical harmonics, we can evaluate the integrals of §2 and get simple expressions for the various coefficients.

Our integrals are all of the form

$$I = \int (\partial f_0 / \partial E) F(\underline{k}) dV,$$

where  $dV = k^2 \sin \theta dk d\theta d\varphi$  is an element of volume in  $\underline{k}$ -space. If we use as our independent variables  $E$ ,  $\theta$  and  $\varphi$ , this becomes

$$I = \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \frac{\partial f_0}{\partial E} F(\underline{k}) k^2 \sin \theta \left\{ \frac{\partial \underline{k}}{\partial E} \right\}_{\theta, \varphi} dE d\theta d\varphi.$$



We can do this since  $E$  is a monotonic function of  $k$  in the cases in which we are interested. Near the surface of the Fermi distribution all the factors in the integrand vary slowly compared to  $\partial f_0/\partial E$ , while elsewhere  $\partial f_0/\partial E$  is practically zero. Hence

$$I = - \int_0^{2\pi} \int_0^\pi \left[ \frac{\partial k}{\partial E} F(\underline{k}) k^2 \right]_{E=E_0} \sin \theta d\theta d\varphi, \quad (11)$$

where  $E_0$  is the energy at the surface of the Fermi distribution.

The partial derivatives that we find in our integrands can be changed to the new variables by means of the following formulas from the calculus:

$$\begin{aligned} Ek_1 = & (k \sin^2 \theta \cos \varphi - k_0 \sin \theta \cos \theta \cos \varphi \\ & + k_\varphi \sin \varphi)(kk_E \sin \theta)^{-1}, \end{aligned}$$

$$\begin{aligned} Ek_2 = & (k \sin^2 \theta \sin \varphi - k_0 \sin \theta \cos \theta \sin \varphi \\ & - k_\varphi \cos \varphi)(kk_E \sin \theta)^{-1}, \end{aligned}$$

$$Ek_3 = (k \cos \theta + k_0 \sin \theta)(kk_E)^{-1},$$

where  $Ek_1$  means the partial of  $E$  with respect to  $k_1$ , keeping  $k_2$  and  $k_3$  constant; while  $k_E$  means the partial of  $k$  with respect to  $E$ , keeping  $\theta$  and  $\varphi$  constant.

Now the lattices of all the monovalent metals have cubic symmetry. Consequently when we expand  $k(E, \theta, \varphi)$  and  $\tau(E, \theta, \varphi)$  in series of surface harmonics, we need include only those surface harmonics that have cubic symmetry. The first two such surface harmonics are

$$Y_0^c = 1$$

and  $Y_4^c = P_4(\cos \theta) + \cos 4\varphi P_4^4(\cos \theta)/168$ ;

the next is of the sixth degree.  $P_n^m$  is Ferrers' associated Legendre function. Neglecting terms of the sixth degree and higher in our expansion, we write

$$\begin{aligned} k &= \alpha_0(E) + \alpha_1(E)Y_4^c, \\ \tau &= \tau_0(E) + \tau_1(E)Y_4^c. \end{aligned} \tag{12}$$

Let us now transform the integrals of Eqs. (6) by the use of Eqs. (11) and (12). If we expand  $[\alpha_0(E) + \alpha_1(E)Y_4^c]^n$ ,  $[\alpha_0'(E) + \alpha_1'(E)Y_4^c]^n$ , and  $[\tau_0(E) + \tau_1(E)Y_4^c]^n$  by the binomial expansion, all the integrations can actually be carried out by means of formulas given by Gaunt [6]. If we write

$$a = \alpha_0(E_0), \quad a' = \left. \frac{d\alpha_0(E)}{dE} \right|_{E=E_0}, \quad t = \tau_0(E_0),$$

$$A = \alpha_1(E_0)/\alpha_0(E_0), \quad B = \frac{1}{a'} \left. \frac{d\alpha_1(E)}{dE} \right|_{E=E_0},$$

$$T = \tau_1(E_0)/\tau_0(E_0),$$

and neglect the cubes of A, B and T compared to unity, we get

$$\begin{aligned}
 I_1 = I_2 = I_3 &= (4\pi/3)(t/a')a^2 \left\{ 1 + (4/21) \right. \\
 &\quad \left. \times [21A^2 + 2A(T-B) - B(T-B)] \right\}, \\
 I_4 &= (4\pi/3)^2(4/77)(t/a')^4 a^2 \\
 &\quad \times \left\{ 597A^2 + 46A(T-B) + 37(T-B)^2 \right\}, \\
 I_5 &= (4\pi/3)(80/231)(t/a')^3 \left\{ 3A + T-B \right\}^2, \tag{13}
 \end{aligned}$$

$$\begin{aligned}
 I_6 &= (4\pi/3)(t/a')^3 \\
 &\quad \times \left\{ 1 + (4/231) [2220A^2 + 600A(T-B) \right. \\
 &\quad \left. - 33B(T-B) + 532(T-B)^2] \right\},
 \end{aligned}$$

$$\begin{aligned}
 I_7 &= (4\pi/3)(t/a')^2 a \\
 &\quad \times \left\{ 1 + (4/21) [30A^2 + 22A(T-B) \right. \\
 &\quad \left. - 2B(T-B) + (T-B)^2] \right\}.
 \end{aligned}$$

Substitution of these values in Eqs. (7)-(10) gives

$$\begin{aligned}
 \sigma &= (4\epsilon^2/3h^2)(t/a')a^2 \left\{ 1 + 4/21 \right. \\
 &\quad \left. \times [21A^2 + 2A(T-B) - B(T-B)^2] \right\} \tag{14}
 \end{aligned}$$

$$R = - (3\pi^2/c\epsilon a^3) \left\{ 1 + (4/21) \right. \\ \left. \times [-12A^2 + 18A(T-B) + (T-B)^2] \right\}, \quad (15)$$

$$B_t = (4/77) (3\pi^2\sigma/c\epsilon a^3)^2 \\ \times \left\{ 597A^2 + 46A(T-B) + 37(T-B)^2 \right\}, \quad (16)$$

$$B_\chi = (80/231) (3\pi^2\sigma/c\epsilon a^3)^2 \left\{ 3A + T-B \right\}^2. \quad (17)$$

We have eliminated  $t$  from the expressions for  $B_t$  and  $B_\chi$  by introducing  $\sigma$  from Eq. (14). We are to regard  $\sigma$  as being determined by experiment.

### §5. Discussion of Results

In the evaluation of these integrals we have made three approximations. In the integration over  $E$  we have, as usual, assumed complete degeneracy. This should not introduce any appreciable error since attempts to explain the change of resistance on a free electron model by using the second approximation in the integration lead to a result that is too small by a factor of about  $10^4$ . We have stopped at the second term in our expansions in surface harmonics and at the square terms in our binomial expansions of  $k$ ,  $k'$  and  $\tau$ . If it seemed desirable, more terms could be included in each expansion, but it does not seem likely that the general results would be changed much. Moreover, these approximations seem to correspond, more or less, to those made by Jones and Zener.

The range of validity of our theory is limited by the condition  $eHv/2mc \ll 1$ . If we introduce the expression given by Wilson [18], p. 161, for the conductivity,  $\sigma = ne^2\tau/m$ , we find that we must require that  $\sigma H \ll ne/m$ .  $n$  is the number of electrons per unit volume. Using the numerical values for silver at ordinary temperatures we find that  $H = 10^5$  gauss is about the upper limit of validity of our theory. Since  $\frac{\Delta\rho}{\rho}$  is proportional to  $(\sigma H)^2$ , it is evident that we do not necessarily improve the accuracy with which we measure  $B_t$  and  $B_l$  if we make our measurements at very low temperatures where a given field produces a much greater change in resistance than at high temperatures; we may only go outside the range of validity of our theory. It is also more difficult to define a relaxation time at low temperatures. It would seem that the best procedure, from the point of view of this theory, is to work at as high field strengths as are available and at temperatures that are high enough so that the theory is valid.

Reasonable values of the parameters, based on Jones and Zener's work on lithium, give the correct orders of magnitude when inserted in the expressions (14)-(17). The consideration of the departures from spherical symmetry have a negligible influence on  $\sigma$  and  $R$ , but provide the essential part of  $B_t$  and  $B_l$ .

Since  $t$  and  $T$  always enter in the combinations  $t/a'$  and  $(T-B)$ , we get nothing by putting in a relaxation time that varies with direction that we could not obtain by suit-

able choice of the shape of the surfaces of constant energy. However, the extra parameters would give a means of getting better agreement between theory and experiment if the shape of the energy surfaces were given by other considerations.

If we consider the value of  $B_t/B_l$  given by Eqs. (16) and (17), we find that this ratio cannot be less than the value, 4.08, obtained when  $A/(T-B) = 1/6$ , and that if  $A/(T-B)$  does not lie between -0.07 and 5.5,  $B_t/B_l$  will be larger than 9. This disagrees with Jones and Zener's theoretical results and with the experimental results; in each the ratios are approximately one. There seem to be two ways of explaining this. One can say that the experimental results are not to be trusted, or one can say that some point has been overlooked in the development of the theory of magnetic effects in metals.

#### §6. Breakdown of Ohm's Law

Although we have treated the relaxation time in the customary manner, it may be that here is the source of our difficulties. In our expansion, we have included terms in  $\tau$  and  $\tau^3$ . Now Wilson [18] proves on page 208 that a relaxation time can be defined at absolute temperatures,  $T$ , that are large compared to the Debye characteristic temperature,  $\theta$ , provided one neglects terms of order  $(\theta/T)^2$  compared to the leading term. He also finds that the relaxation time is of the form

$$\tau = C^*kE\theta/T \quad (18)$$

where  $C'$  is a constant. Hence if Wilson's derivation gives the upper limit of validity of the concept of relaxation time, we must neglect  $\tau^3$  compared to  $\tau$  and therefore cannot deal with the change of resistance by this method. However, Wilson's treatment gives directly only sufficient conditions and it may be that they are not necessary.

Since direct treatment of this problem seems difficult, we will try to learn something of the range of powers of  $\tau$  over which the concept of relaxation time is valid by considering another problem in which both  $\tau$  and  $\tau^3$  enter. In order to calculate theoretically the current density at which Ohm's law commences to break down, one must go farther than the first approximation to the dependence of the current on the electric field. Guth and Mayerhöfer [7] have proved that in the Lorentz model of metallic conduction with its fixed metal ions the fundamental equation is not soluble in the second approximation. The reason that the integral equation for the second approximation has no solutions whatever is that the exchange of energy between the electrons and the lattice is omitted in the Lorentz model and, in the second approximation, a stationary state does not exist. By using the fundamental equations of the wave-mechanical theory of conductivity, Guth and Mayerhöfer are able to go to higher approximations. They find that a current density of  $10^9$  amp./cm<sup>2</sup> causes a one per cent deviation from Ohm's law, the conductivity decreasing with increasing field.

If, rather than making Lorentz's detailed assumptions, one assumes only that a relaxation time exists, the problem is much simplified. Boltzmann's equation, (1), becomes  $\mathcal{E}\tau(\underline{k})\partial f/\partial k_1 - \hbar[f - f_0] = 0$  if the electric field is directed in the x-direction and has the magnitude  $\mathcal{E}$  and if the magnetic field is zero. Let us expand  $f$  in a power series in  $\mathcal{E}^n$ , as we considered doing in the development of equation (3). When we put  $f = \sum_{n=0}^{\infty} f_n \mathcal{E}^n$  in Boltzmann's equation and equate to zero the coefficient of  $\mathcal{E}^n$ , we find that  $f_n(\underline{k}) = [(\mathcal{E}/\hbar)\tau(\underline{k})\partial/\partial k_1]^n f_0(\underline{k})$ . Since we will take  $f_0(\underline{k})$ , the distribution function when there is no field, to be the Fermi distribution, we may regard  $f(\underline{k})$  as being completely determined. We will ignore for the present the possible non-convergence of the series.

The current is in the same direction as the field and from (2) and (5) is

$$J = - (\epsilon/4\pi^3\hbar) \int [\partial E(\underline{k})/\partial k_1] f(\underline{k}) dV = (\epsilon/4\pi^3\hbar) \sum_{n=0}^{\infty} (\mathcal{E}/\hbar)^n \mathcal{E}^n I_n$$

$$\begin{aligned} \text{where } I_n &= - \int (\partial E/\partial k_1) [\tau(\underline{k})\partial/\partial k_1]^n f_0(\underline{k}) dV \\ &= (-1)^n \int (\partial f_0/\partial k_1) \tau [(\partial/\partial k_1)\tau]^{n-1} (\partial E/\partial k_1) dV. \end{aligned}$$

The integral  $I_n$  has been transformed by means of  $n-1$  integrations by parts. If  $\tau$  is a constant,  $I_n = 0$  unless  $n = 1$ , and consequently Ohm's law is exact. But if we consider the free



electron case in which  $E = \hbar^2 k^2 / 2m$ , which is the case considered by Guth and Mayerhöfer, and if we determine  $\tau$  from (18) so that  $\tau = Ck^3$ , we find that  $I_n$  is zero if  $n$  is even but not if  $n$  is odd. It can be seen readily enough by carry-out the repeated differentiation and keeping only the highest power of  $k$  that  $(\partial f_0 / \partial k_1) \tau [(\partial / \partial k_1) \tau]^{2r} (\partial E / \partial k_1)$  is greater than  $(\partial f_0 / \partial k_1) C^{2r+1} (\hbar^2 / 2m) 6 \cdot 10 \cdot 14 \cdots (4r+2) k_1^{4r+3}$ . By using (11) we find that  $\int (\partial f_0 / \partial k_1) k_1 k^{4r+3} dV = - (4\pi/3) (2mE_0 / \hbar)^{2r+3}$ .

Therefore  $I_{2r+1}$  is greater than  $(4\pi/3) 6 \cdot 10 \cdot 14 \cdots (4r+2) C^{2r+1} (2mE_0 / \hbar)^{2r+3}$ . From this it is evident that our series for  $J$  diverges. Further calculation shows that the first four non-zero terms of this series are

$$J = \frac{4m\epsilon E_0^2}{\pi^2 \hbar^2} \left\{ \frac{1}{3} C^2 \left( \frac{2m\epsilon E_0}{\hbar^3} \right) + \frac{32}{5} C^3 \left( \frac{2m\epsilon E_0}{\hbar^3} \right)^3 + \frac{2880}{7} C^5 \left( \frac{2m\epsilon E_0}{\hbar^3} \right)^5 + 57,394 C^7 \left( \frac{2m\epsilon E_0}{\hbar^3} \right)^7 + \dots \right\}$$

We can use the relation  $J = \sigma E$  to give  $C$  in terms of  $\sigma$ , the conductivity for small fields. Substituting this value of  $C$  back in the series gives

$$J = \sigma E + 3^3 \cdot \frac{32}{5} \left( \frac{\pi^2 \hbar^2}{4m\epsilon E_0^2} \right)^2 E^3 + 3^5 \cdot \frac{2880}{7} \sigma^5 \left( \frac{\pi^2 \hbar^2}{4m\epsilon E_0^2} \right)^4 E^5 + 3^7 \cdot 57,394 \sigma^7 \left( \frac{\pi^2 \hbar^2}{4m\epsilon E_0^2} \right)^6 E^7 + \dots \quad (19)$$

If the second term is one per cent of the first, the third and fourth terms are negligible. If, in this case, we regard the series as an asymptotic expansion or if we assume that our treatment gives the first two terms of the series accurately enough for our purpose but that the diverging terms should be omitted, we can readily calculate the field strength at which deviations from Ohm's law become noticeable. We take the same values of the constants as do Guth and Mayerhöfer,  $E_0 = 5.5$  e.v. and  $\sigma = 6 \times 10^{17}$  e.s.u., and the same criterion for an observable deviation from Ohm's law, that the second term in the series be one one hundredth of the first term. Guth and Mayerhöfer find that such an effect appears when  $\mathcal{E} = 5$  e.s.u. and  $J = 10^9$  amp./cm<sup>2</sup>, the conductivity decreasing. Our method leads to the conclusion that a deviation is first noticeable when  $\mathcal{E} = 160$  e.s.u. and  $J = 3 \times 10^{10}$  amp./cm., the conductivity increasing with the field. Neither result is contradicted by experiment since, as shown by Barlow [2], all that experiment yields is that there is no apparent deviation from Ohm's law for current densities up to  $2 \times 10^6$  amp./cm<sup>2</sup>.

Since Guth and Mayerhöfer's treatment is entirely different from ours, it would be very difficult to say whether the discrepancy between their results and ours is due to the fact that they find the deviation due to one cause while we consider another, in which case their result

is the only one of practical significance; or whether there is some flaw in one of the derivations. It is evident on physical grounds that our method will give a conductivity that increases with the field so that we have not made a mistake in sign. One sees this by noting that the relaxation time, the average time between collisions if we use a crude interpretation, increases with the velocity. Hence, in addition to the current due to the change of the velocity of the electrons in the electric field, there tends to be additional current due to the fact that electrons that are going in the direction in which the field urges them travel farther between collisions than electrons going in the opposite direction. This occurs because electrons in the first class are speeded up by the field and hence get longer mean free times while electrons in the second class are slowed down and hence get shorter mean free times. This gives a second order increase in the conductivity.

While this discussion has not settled the question as to whether or not it is proper to include  $\tau^3$  in an expression that includes  $\tau$ , it certainly has not allayed our suspicions that such a procedure may not yield valid results.

## THE TIGHTLY BOUND ELECTRON APPROXIMATION

### §7. Introduction

In considering the change of resistance in a magnetic field, we treated the magnetic field as a perturbation that caused the electrons to change from state to state, the states being those found when there was no field. We found that although magnetic effects cancel out in the first approximation when we consider all the electron states, magnetic forces were large and would greatly affect the states of the individual electrons. Hence if we could work with states that were exact in a magnetic field, we should expect to get a more satisfactory treatment of the effect of a magnetic field on conduction electrons. This can best be done if we work with the tightly bound electron approximation invented by Bloch [3]. All that need be done to adapt this treatment to a magnetic field is to use, in the linear combination of wave functions of isolated atoms, wave functions for atoms in a magnetic field in place of the usual wave functions. Most of the changes that result from this are due to the necessity of making a gauge transformation when an atom is translated in a uniform magnetic field. As a simple, satisfactory example, we work out in §8 the general theory of this problem for a two-dimensional lattice with square cells. The necessary integrals are evaluated and the problem is reduced to the solution of a set of

simultaneous equations. The case in which the magnetic field is zero is solved in §9 by inspection, by means of matrix manipulation, and by converting the problem into a difference equation. In §10 the way in which all these methods of solution break down when a magnetic field is present is considered. In these last two sections we study various boundary conditions and find that cyclic boundary conditions are possible in a magnetic field only if the field strength is restricted to certain discrete values. In an attempt to learn something of the properties that a solution of the general problem would have, we solve completely in §11 the problem that arises from a two by two lattice and calculate the magnetic susceptibility of such a crystal, or molecule. We find that the susceptibility is of the right order of magnitude, but that its sign and exact size depend in a very sensitive manner on the value of the lattice constant. Further consideration of the tightly bound electron approximation leads us to our final problem, <sup>the</sup> effect of a magnetic field on the validity of Floquet's theorem.

### §8. General Theory

The cause of most of the difficulties that arise in this problem is the fact that if an atom is displaced from one position to another, its wave function is not obtained by a translation of coordinates but by such a translation plus a gauge transformation. We will always deal with a uniform

magnetic field in the z-direction whose vector potential is  $\underline{A} = (-Hy/2, Hx/2, 0)$ . The Hamiltonian for an electron in this magnetic field and an electrostatic field in which the potential energy of the electron is  $V$  has the form

$$\mathcal{H}_{op} = \frac{1}{2m} [-\hbar^2 \nabla^2 + (\frac{\hbar e H}{10}) (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) + (\frac{e H}{2c})^2 (x^2 + y^2)] + V. \quad (20)$$

We have neglected spin. If  $\psi(x, y, z)$  is an eigenfunction of the equation  $(\mathcal{H}_{op} - E)\psi = 0$  when the potential energy is  $V(x, y, z)$ , then

$$\psi(x-\xi, y-\eta, z-\zeta) \exp[i(eH/2c\hbar)(x\eta - y\xi)] \quad (21)$$

is an eigenfunction when the potential energy is  $V(x-\xi, y-\eta, z-\zeta)$ ; i.e., the atom has been translated a distance  $(\xi, \eta, \zeta)$ . Both eigenfunctions have the eigenvalue  $E$ . These statements are readily verified by direct substitution in Schrödinger's equation.

In this discussion of the effect on the wave function of placing an atom at various points in a uniform magnetic field, we have considered only exact solutions of Schrödinger's equation. However, one does not usually work with exact solutions when a magnetic field is present, since then they are difficult to find and too complicated to manipulate. Instead, when dealing with an atom at the origin, one writes

$$\mathcal{H}'_{op} = \mathcal{H}' + V(x, y, z) = \mathcal{H}'' + (1/2m)(eH/2c)^2(x^2 + y^2) + V(x, y, z)$$

and solves the equation

$$(\mathcal{H}'' + V - E^0)\psi^0 = 0. \quad (22)$$

Since the omitted term,  $(1/2m)(eH/2c)^2(x^2 + y^2)\psi^0$ , is small for an atom at the origin, this is a satisfactory approximation. The corresponding approximation to the wave function for an electron in an atom at  $\underline{a}_h = (a_{h1}, a_{h2}, a_{h3})$  is taken by analogy with (21) to be

$$\psi_{\underline{h}}^0(\underline{r}) = \psi^0(\underline{r} - \underline{a}_h) \exp[(ieH a_{h2} / 2c\hbar)(x_{h2} - y_{h1})] \quad (23)$$

where  $\underline{r}$  is the radius vector from the origin. That the approximation is the same for all atoms may be seen by introducing relative coordinates  $\underline{r}_{\underline{h}} = \underline{r} - \underline{a}_h = (x_{\underline{h}}, y_{\underline{h}}, z_{\underline{h}}) = (x - a_{h1}, y - a_{h2}, z - a_{h3})$ . One finds that

$$[\mathcal{H}' + V(\underline{r}_{\underline{h}}) - E^0]\psi_{\underline{h}}^0(\underline{r}) = (1/2m)(eH/2c)^2(x_{\underline{h}}^2 + y_{\underline{h}}^2)\psi_{\underline{h}}^0(\underline{r}). \quad (24)$$

In considering the changes produced in the tight binding approximation by a magnetic field in the z-direction, all essential features will be evident if we consider a two-dimensional square lattice in the xy-plane. The transition to the general three-dimensional lattice is just the same as in the case in which there is no field. We will suppose that the atoms are located at the points  $\underline{a}_h$ , where  $a$  is the lattice constant and the components of  $\underline{h}$  are the integers,  $(h_1, h_2, 0)$ .

The wave function of a single electron in the lattice is then written

$$\Psi(\underline{r}) = \sum_{\underline{h}} c_{\underline{h}} \psi_{\underline{h}}^0(\underline{r}) \quad (25)$$

where  $\psi_{\underline{h}}^0(\underline{r})$  is defined by (23). The sum is over all the atoms of the lattice.

We find the constants,  $c_{\underline{h}}$ , and an approximation to the energy,  $E$ , from the equations

$$\int \psi_{\underline{g}}^{0*} (\mathcal{H} + V_L - E) \Psi \, d\tau = 0 \quad (26)$$

$V_L$  is the potential energy of an electron in the lattice, including the self-consistent field if possible, and  $d\tau = dx dy dz$  is the element of volume in coordinate space.  $\underline{f}$  and  $\underline{g}$  will be taken, like  $\underline{h}$ , to be vectors with integral components.

Let  $V_{\underline{h}}$  be the potential of an isolated atom at  $a\underline{h}$ , or, in general, any potential that approximates closely to  $V_L$  in the neighborhood of the atom at  $a\underline{h}$  and for which (22) can be solved. Let us define  $V_{\underline{h}}'$  as  $V_L - V_{\underline{h}}$ . This enables us to use (25) and (24) to transform (26) to

$$\sum_{\underline{h}} c_{\underline{h}} \int \psi_{\underline{g}}^{0*} \left[ E^0 - E + V_{\underline{h}}' + \frac{1}{2m} \left( \frac{\epsilon H}{2c} \right)^2 (x_{\underline{h}}^2 + y_{\underline{h}}^2) \right] \psi_{\underline{h}}^0 \, d\tau = 0.$$

This is of the form

$$\sum_{\underline{h}} A_{\underline{g}, \underline{h}} c_{\underline{h}} = 0 \quad (27)$$



where  $A_{\underline{g}, \underline{h}}$  is the above integral. If we neglect possible complications at the edge of the crystal,  $V_{\underline{h}}$  will depend only on  $\underline{r}_{\underline{h}}$ . Therefore the integral is of the form  $A_{\underline{g}, \underline{h}} = \int \psi_{\underline{g}}^{0*} f(\underline{r}_{\underline{h}}) \psi_{\underline{h}}^0 d\tau$ . By using (23) this becomes

$$A_{\underline{g}, \underline{h}} = e^{iB(\underline{g}_1 h_2 - \underline{g}_2 h_1)} \int \psi_{\underline{g}}^{0*}(\underline{r}_{\underline{h}} - a[\underline{g} - \underline{h}]) f(\underline{r}_{\underline{h}}) \psi_{\underline{h}}^0(\underline{r}_{\underline{h}}) e^{-i\frac{B}{a}[x_{\underline{h}}(g_2 - h_2) - y_{\underline{h}}(g_1 - h_1)]} d\tau$$

$$= e^{iB(\underline{g}_1 h_2 - \underline{g}_2 h_1)} A(\underline{g} - \underline{h})$$

where  $B = \epsilon H a^2 / 2c\hbar$ , and (27) becomes

$$\sum_{\underline{h}} e^{iB(\underline{g}_1 h_2 - \underline{g}_2 h_1)} A(\underline{g} - \underline{h}) c_{\underline{h}} = 0. \quad (28)$$

Our attempts to solve (28) will be more understandable if we first find the numerical value of the integral for  $A(\underline{h})$ . It can be evaluated more easily if we break it into parts, writing

$$A(\underline{h}) = [E^0 - E]\Delta(\underline{h}) + V(\underline{h}) + R(\underline{h}) \quad (29)$$

and

$$\Delta(\underline{h}) = \int \psi^{0*}(\underline{r} - a\underline{h}) \psi^0(\underline{r}) e^{-i\frac{B}{a}(xh_2 - yh_1)} d\tau$$

$$V(\underline{h}) = \int \psi^{0*}(\underline{r} - a\underline{h}) V_{\underline{0}}^0(\underline{r}) \psi^0(\underline{r}) e^{-i\frac{B}{a}(xh_2 - yh_1)} d\tau \quad (30)$$

$$R(\underline{h}) = \frac{1}{2m} \left(\frac{\epsilon H}{2c}\right)^2 \int \psi^{0*}(\underline{r} - a\underline{h}) (x^2 + y^2) \psi^0(\underline{r}) e^{-i\frac{B}{a}(xh_2 - yh_1)} d\tau$$

Each of these integrals contains the product  $\psi^{0*}(\underline{r}-a\underline{h})\psi^0(\underline{r})$  and will therefore approach zero rapidly as  $\underline{h}$  increases in length. In fact, the tight binding approximation is only appropriate when we can neglect all integrals unless  $\underline{h}$  is either a zero or a unit vector; i.e., unless one component of  $\underline{h}$  is zero and the other is either zero or one. We will further simplify the problem by considering only s states so that  $\psi^0(\underline{r})$  will be spherically symmetrical. It follows that, if  $\underline{i}$  and  $\underline{j}$  denote the usual unit vectors,  $\Delta(\underline{i})=\Delta(-\underline{i})=\Delta(\underline{j})=\Delta(-\underline{j})=\Delta_1$ ,  $\Delta(\underline{0})=\Delta_0$ , and for all other values of  $\underline{h}$ ,  $\Delta(\underline{h})=0$ . Similar equations hold for  $R(\underline{h})$  and  $V(\underline{h})$ . Since our atomic wave functions are normalized,  $\Delta_0=1$ , leaving only the five integrals  $\Delta_1$ ,  $R_0$ ,  $R_1$ ,  $V_0$ , and  $V_1$  to be evaluated.

To get an idea as to the numerical values of these integrals, we must decide on the function  $V(\underline{r})$  to be taken as the potential of an isolated atom in the solution of (22) and on the function  $V'_{\underline{h}}(\underline{r})$  to be substituted in the integral for  $V(\underline{h})$ . It will be sufficient for our purposes to take  $V=-\epsilon^2/r$ ; i.e., the potential of a hydrogen atom. The wave functions will be the hydrogen wave functions and we will take  $\psi^0$  to be the wave function for the 1s state so that

$$\psi^0 = (1/\sqrt{\pi a_0^3}) e^{-r/a_0}, \quad a_0 = \hbar^2/m\epsilon^2 = .527 \times 10^{-8} \text{ cm.},$$

$$E^0 = -\epsilon^2/2a_0 = -2.18 \times 10^{-11} \text{ ergs.} \quad \text{We will assume that}$$

$V'_h = [\sum_{\underline{g} \neq \underline{h}} V_{\underline{g}}] - V_h$ , thus implying that  $V'_h$  is the sum of the Coulomb potentials of all the atoms of the lattice except the atom at  $a\underline{h}$ . When we substitute this in  $V_0$ , the only terms that contribute anything will be those due to the four nearest atoms, and when we substitute in  $V_1 = V(\underline{i})$ , the only term that contributes appreciably is that due to the atom at  $a\underline{i}$ . Hence

$$V_0 = 4 \int \psi^{0*}(\underline{r}) (-e^2/|\underline{r}_1|) \psi^0(\underline{r}) d\tau$$

$$V_1 = \int \psi^{0*}(\underline{r}_1) (-e^2/|\underline{r}_1|) \psi^0(\underline{r}) \exp[iBy/a] d\tau \quad (31)$$

where  $\underline{r}$  refers to the radius vector drawn from the origin,  $\underline{r}_1$  to that drawn from the atom to the right of the origin, and  $|\underline{r}_1|$  is the magnitude of the vector  $\underline{r}_1$ .

To evaluate these integrals we use confocal elliptic coordinates as given by Pauling and Wilson [11], p. 444. We let  $x = a(\xi\eta+1/2)$ ,  $y = \frac{a}{2} \sqrt{\xi^2-1} \sqrt{1-\eta^2} \sin\phi$ , and  $z = -\frac{a}{2} \sqrt{\xi^2-1} \sqrt{1-\eta^2} \cos\phi$ . It follows that  $r + |\underline{r}_1| = a\xi$ ,  $|\underline{r}_1| = \frac{a}{2}(\xi-\eta)$ , and  $d\tau = (\frac{a}{2})^3 (\xi^2-\eta^2) d\xi d\eta d\phi$ . In terms of these variables we find that

$$\Delta_1 = \int \psi^{0*}(\underline{r}_1) \psi^0(\underline{r}) e^{iBy/a} d\tau = \frac{1}{\pi} \left(\frac{1}{a_0}\right)^3 \int e^{-(|\underline{r}_1|+r)/a_0} e^{iBy/a} d\tau$$

$$\begin{aligned}
 &= \frac{1}{8\pi} \left(\frac{a}{a_0}\right)^3 \int_1^\infty \int_{-1}^1 \int_0^{2\pi} e^{-a\xi/a_0} \left[1 - \frac{1}{8B^2}(\xi^2-1)(1-\eta^2)\right] (\xi^2-\eta^2) d\phi d\eta d\xi \\
 &= e^{-\rho} \left(\frac{\rho^2}{3} + \rho + 1\right) - \frac{B^2 e^{-\rho}}{30} \left(\rho + 6 + \frac{15}{\rho} + \frac{15}{\rho^2}\right)
 \end{aligned}$$

where  $\rho = a/a_0$ . In expanding  $e^{iBy/a}$  in a power series, terms involving odd powers of  $y$  were omitted since they would not survive integration over  $\phi$  and terms involving higher powers than the third were omitted since we are not interested in terms beyond those that are quadratic in  $H$  and hence in  $B$ . That this power series expansion is valid is evident since  $y$  may be considered to be of the order of magnitude of  $a$ ,  $B$  is about  $10^{-8}H$ , and we are concerned with magnetic fields not greater than  $10^5$  gauss. In a similar manner we can find that

$$\begin{aligned}
 V_0 &= 4E^0 \left[ \frac{2}{\rho} - 2e^{-2\rho} \left(1 + \frac{1}{\rho}\right) \right] \\
 V_1 &= E^0 e^{-\rho} \left[ 2(\rho+1) - \frac{B^2}{2\rho^2} \left(\frac{\rho^2}{3} + \rho + 1\right) \right] \\
 R_0 &= \frac{1}{2m} \left(\frac{\epsilon H}{2c}\right)^2 2a_0^2 \\
 R_1 &= \frac{1}{2m} \left(\frac{\epsilon H}{2c}\right)^2 \frac{a_0^2}{30} e^{-\rho} [3\rho^4 + 13\rho^3 + 33\rho^2 + 60\rho + 60] \\
 \Delta_0 &= 1 \\
 \Delta_1 &= e^{-\rho} \left(\frac{\rho^2}{3} + \rho + 1\right) - \frac{B^2 e^{-\rho}}{30} \left(\rho + 6 + 15 \frac{1}{\rho} + 15 \frac{1}{\rho^2}\right).
 \end{aligned} \tag{32}$$

We will calculate the numerical values of these integrals for the case in which the lattice constant is

$a = 3.12 \times 10^{-8}$  cm. and  $\rho = 6$ . This value of  $\rho$  is chosen although it leads to less overlapping of wave functions than occurs in crystals such as those of lithium since if  $\rho$  is assumed to be smaller than 6 so that there will be more overlapping, our approximations become unsatisfactory. We should, however, be able to determine the essential features of this method of approach by taking  $\rho = 6$ . We find that

$$\begin{aligned}V_0 &= -2.90 \times 10^{-11} \text{ ergs,} \\V_1 &= -7.56 \times 10^{-13} + 8.25 \times 10^{-31} H^2 \text{ ergs,} \\R_0 &= 1.96 \times 10^{-30} H^2 \text{ ergs,} \\R_1 &= 6.71 \times 10^{-31} H^2 \text{ ergs,} \\ \Delta_0 &= 1, \\ \Delta_1 &= 4.71 \times 10^{-2} - 7.14 \times 10^{-20} H^2, \\ E^0 &= -2.18 \times 10^{-11} \text{ ergs.}\end{aligned} \tag{33}$$

It might appear that we should use in place of the 1s hydrogen wave function, a wave function such as that given by Pauling and Wilson [11], p. 247, that represents the lowest state of lithium. Then by considering a body-centered cubic lattice, we might hope to get results that would be valid for actual lithium crystals. No additional difficulties in principle are involved in this program; and although the calculations are made considerably more complicated, they are not

unreasonably long. However, in all actual metals the atoms are so close together that the interactions are large and the tight binding approximation gives but a rough idea as to the actual behavior of the crystal. We ought to be able to get as satisfactory results in a much clearer manner by considering the simplest possible case. It might be advisable, as suggested by Bardeen and Van Vleck [1], to use wave functions of the form,  $\exp[-cr]/r$ , that result from screened atom potentials rather than functions of the form,  $\exp[-cr]$ , that result from hydrogenic potentials. In this way the magnetic moment as calculated from the energy would be more nearly equal to that calculated from the current.

Thus far we have considered only atoms that are inside the lattice and have not concerned ourselves with atoms on the boundary. The only change that need be made in our treatment because of the boundary atoms is a modification of  $V'_{\underline{h}}$  and hence of  $V(\underline{h})$ .

If we consider the approximation used in (31), we see that  $V_1$  is not affected while the factor 4 in the expression for  $V_0$  is replaced by 3 if  $\underline{h}$  refers to a lattice point on the edge of the crystal and by 2 if  $\underline{h}$  refers to a lattice point at a corner.

§9. Solution When There is No Magnetic Field

The condition that the set of homogeneous, simultaneous equations

$$\sum_{\underline{h}} \exp[iB(\underline{g}_1 h_2 - \underline{g}_2 h_1)] A(\underline{g}-\underline{h}) c_{\underline{h}} = 0 \quad (28)$$

possesses solutions determines the possible values for  $E$ , and for each such value there is a set of  $c_{\underline{h}}$ 's that satisfy (28). Before considering the solution of (28), let us first consider the simpler case in which there is no magnetic field. The solution of this problem is, of course well known. The equation,  $\sum_{\underline{h}} A(\underline{g}-\underline{h}) c_{\underline{h}} = 0$ , to which (28) reduces, can be solved either by guessing that the solution is  $\exp[i\underline{h} \cdot \underline{k}]$  and checking, by reducing to diagonal form the matrix  $\|a_{\underline{g}, \underline{h}}\|$  where  $a_{\underline{g}, \underline{h}} = A(\underline{g}-\underline{h})$ , or by solving the difference equation  $\sum_{\underline{h}} A(\underline{h}) c_{\underline{g}-\underline{h}} = 0$ . The fact that  $\underline{g}$  and  $\underline{h}$  are two or three-dimensional vectors with integral components causes no trouble when there is no magnetic field.

If we substitute  $c_{\underline{h}} = e^{i\underline{h} \cdot \underline{k}}$  in  $\sum_{\underline{h}} A(\underline{g}-\underline{h}) c_{\underline{h}} = 0$  and divide by  $e^{i\underline{g} \cdot \underline{k}}$ , our equation is solved provided  $\sum_{\underline{h}} A(\underline{h}) e^{i\underline{h} \cdot \underline{k}} = 0$ . Therefore the energy is determined from the equation

$$E \sum_{\underline{h}} \Delta(\underline{h}) e^{i\underline{h} \cdot \underline{k}} = \sum_{\underline{h}} [E^0 \Delta(\underline{h}) + V(\underline{h}) + R(\underline{h})] e^{i\underline{h} \cdot \underline{k}} \quad (34)$$

From this it appears that we get a solution no matter what  $\underline{k}$  is, and that by proper choice of  $\underline{k}$  we can get any of an infinite number of energies for the system. This infinite number

of solutions corresponds to the fact that we have said nothing about boundary conditions for our crystal lattice but have tacitly assumed that it was an infinite crystal. If we wish to have only a finite number of solutions, we must specify our boundary conditions. The simplest conditions for this case are obtained by requiring that  $c_{\underline{h}+\underline{g}G} = c_{\underline{h}}$  where  $G$  is the number of atoms on a side of the square that forms one cycle. We call these conditions cyclic boundary conditions since they require that  $\psi(\underline{r}+\underline{g}G) = \psi(\underline{r})$ . They restrict  $\underline{k}$  so that  $\underline{k}G/2\pi$  is a vector with integral components lying between 1 and  $G$ , inclusive, and give us a set of  $G^2$  solutions. It is usually easier to treat other boundary conditions by either the matrix or the difference equation method than to try to get a solution by inspection.

In using the matrix method, we must include the boundary conditions when setting up the matrix. If we take the cyclic conditions  $c_{\underline{h}+\underline{f}G} = c_{\underline{h}}$ , we get the particularly simple matrix that results from the set of equations

$$\sum_{\underline{h}}^G \sum_{\underline{f}}^{\infty} A(\underline{g}-\underline{h}-\underline{f}G) = 0.$$

The superscripts on the summations indi-

cate that the two components of  $\underline{h}$  run from 1 to  $G$  while those of  $\underline{f}$  run from  $-\infty$  to  $+\infty$ . Although this set contains an infinite number of equations since the components of  $\underline{g}$  run from  $-\infty$  to  $+\infty$ , each equation is the same as some member of the subset obtained when the components of  $\underline{g}$  lie between 1 and  $G$ . Hence we can restrict  $\underline{g}$  to this range and get  $G^2$  homogeneous,



simultaneous equations in the  $G^2$  unknowns,  $c_{\underline{h}}$ . If, instead of considering an infinite lattice with cyclic boundary conditions, we considered a finite, square crystal containing  $G$  atoms on a side,  $\underline{g}$  and  $\underline{h}$  each run over the  $G^2$  values corresponding to the  $G^2$  atoms of the crystal, and again we get from  $\sum_{\underline{h}} A(\underline{g}-\underline{h})c_{\underline{h}} = 0$ ,  $G^2$  equations in  $G^2$  unknowns.

Our problem has been reduced to a standard type and we can use standard methods in its solution. The only complication is that the subscripts that identify our  $G^2$  unknowns,  $c_{\underline{h}}$ , are two-dimensional vectors with integral components instead of integers. Similarly  $\underline{g}$ , which by taking on its different values gives the  $G^2$  equations to be solved, is a vector. In considering the formal solution to the set of equations we find that this introduces no changes except that the matrices will be four-dimensional instead of two-dimensional arrays. It is possible to formulate satisfactory rules for the manipulation of such matrices and the determinants derived from them and to carry through the entire solution on this basis. We will find it most convenient to use four-dimensional matrices and determinants throughout the formal treatment where they can be treated and thought of as though they were ordinary matrices and determinants; but to reduce them to ordinary matrices and determinants when we wish to solve any specific problem. If  $A = \|a_{\underline{g},\underline{h}}\|$  is the matrix of the coefficients of the  $c_{\underline{h}}$ 's and  $|A|$  is the determinant of this matrix, then the energy is

determined from the equation  $|A|=0$ . If we can determine a unitary matrix  $M = \|m_{\underline{h}, \underline{f}}\|$  such that  $M^+AM$  is a diagonal matrix whose elements are linear in the energy, the energy is given directly by  $|M^+AM| = 0$ , and the  $c_{\underline{h}}$ 's corresponding to the energy determined from the  $\underline{f}$ 'th row and  $\underline{f}$ 'th column of this determinant are proportional to  $m_{\underline{h}, \underline{f}}$ . The + indicates that  $M^+$  is the adjoint matrix to  $M$ ; that is, rows and columns are interchanged and all elements are replaced by their complex conjugates. If obvious precautions as to the nature of  $M$  are taken, it need not be a unitary matrix.

All this will be clearer if we consider as an example the case in which we have cyclic boundary conditions and only the interactions of an atom with its four nearest neighbors are important. In this case, provided we consider only  $s$  states,  $a_{\underline{g}, \underline{h}} = \sum_{\underline{f}} A(\underline{g}-\underline{h}-\underline{f}G)$  is  $a^0$  if  $\underline{g}=\underline{h}$ , is  $a'$  if  $\underline{g}-\underline{h}-\underline{f}G$  is a unit vector for some  $\underline{f}$  (which must be either a zero or a unit vector), and is zero otherwise. In order to be able to write down the matrix conveniently in this case we must write it as a two-dimensional array. Since  $\underline{g}$  and  $\underline{h}$  are vectors with integral components, there is no intrinsically natural way in which to order their values. Hence we arbitrarily decide always to run through the values of  $\underline{g}$  and  $\underline{h}$  in the order  $(1,1); (1,2) \dots (1,G); (2,1); (2,2) \dots (2,G) \dots (G,1); (G,2) \dots (G,G)$ . The resulting matrix  $A$  is best expressed as a  $G$  by  $G$  matrix each of whose elements is a  $G$  by  $G$  matrix.

$$A = \begin{vmatrix} B & D & 0 & \dots & 0 & D \\ D & B & D & \dots & 0 & 0 \\ 0 & D & B & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & B & D \\ D & 0 & 0 & \dots & D & B \end{vmatrix}, \quad \text{where } B = \begin{vmatrix} a^0 & a' & 0 & \dots & 0 & a' \\ a' & a^0 & a' & \dots & 0 & 0 \\ 0 & a' & a^0 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & a^0 & a' \\ a' & 0 & 0 & \dots & a' & a^0 \end{vmatrix}$$

and D is a G by G diagonal matrix, each of whose diagonal elements is a'. In writing A in this manner, we think of it at first as a kind of chart that enables<sup>us</sup> to write down a G<sup>2</sup> by G<sup>2</sup> matrix whose elements are ordinary numbers; soon we will come to think of A as a genuine G by G matrix whose elements are of a somewhat uncommon type.

If B and D were ordinary numbers, A would be a cyclic matrix and could be reduced to diagonal form by means of the transformation N<sup>+</sup>AN, where N = ||n<sub>f<sub>1</sub>,h<sub>1</sub></sub>|| and n<sub>f<sub>1</sub>,h<sub>1</sub></sub> = e<sup>2πif<sub>1</sub>h<sub>1</sub>/G</sup>. The term on the diagonal in the f<sub>1</sub>'th column of the resulting diagonal matrix is B+2Dcos(2πif<sub>1</sub>/G). Exactly the same procedure can be used in our problem if B and D are matrices and n<sub>f<sub>1</sub>,h<sub>1</sub></sub> is assumed to be a unit matrix multiplied by n<sub>f<sub>1</sub>,h<sub>1</sub></sub> = e<sup>2πif<sub>1</sub>/G</sup>. The G<sup>2</sup> by G<sup>2</sup> matrix that results from the transformation contains nothing but zeros except in G by G blocks along its diagonal. Since each of these blocks is cyclic, it is not very difficult to find a further transformation that will give us a diagonal matrix, the diagonal element in the [(f<sub>1</sub>-1)G+f<sub>2</sub>]'th column being a<sup>0</sup>+2a'cos(2πif<sub>1</sub>/G)+2a'cos(2πif<sub>2</sub>/G). By multiplying together the two transformations used, we find the single equivalent transformation to be M = ||m<sub>f<sub>1</sub>,h<sub>1</sub></sub>|| where

$m_{\underline{f}, \underline{h}} = e^{2\pi i \underline{f} \cdot \underline{h} / G}$ . Hence the set of  $c_{\underline{h}}$ 's that goes with the energy equation  $a^0 + 2a' \cos(2\pi i \underline{f}_1 / G) + 2a'' \cos(2\pi i \underline{f}_2 / G) = 0$  is  $c_{\underline{h}} = C e^{2\pi i \underline{f} \cdot \underline{h} / G}$  where  $C$  is a normalizing constant. If we have cyclic boundary conditions but wish to include the interactions of all atoms,  $a_{\underline{g}, \underline{h}} = \sum_{\underline{f}} A(\underline{g} - \underline{h} - \underline{f}G)$  depends only on  $\underline{g} - \underline{h}$ . Therefore,  $A$  is a block-cyclic matrix, each block being itself cyclic. The same matrix used in the above example transforms  $A$  to diagonal form; but the energy is given by  $\sum_{\underline{h}} A(\underline{h}) e^{2\pi i \underline{h} \cdot \underline{f} / G} = 0$ . This is, of course, equivalent to equation (34). Other types of boundary conditions can usually be conveniently treated by matrix manipulation if, when single letters are substituted for  $G$  by  $G$  blocks of elements, a  $G$  by  $G$  matrix results that can be treated by known methods. This method sometimes breaks down because of the fact that the order of numerical factors does not matter while the order of matrix factors does.

Perhaps the most powerful attack on this problem can be made by transforming  $\sum_{\underline{h}} A(\underline{g} - \underline{h}) c_{\underline{h}} = 0$  into the difference equation  $\sum_{\underline{h}} A(\underline{h}) c_{\underline{g} - \underline{h}} = 0$ . This transformation is formally only a slight change in notation; there is no real change since we try to solve exactly the same set of equations in either case. We have merely noticed that our equations have the same form as the set that is derived from a difference equation and have decided to apply some of the known methods of treating difference equations to our problem. Since we have a linear difference equation with constant coefficients, a particular

solution is found by means of the substitution  $c_{\underline{g}} = e^{i\underline{g}\cdot\underline{k}}$ .  $\underline{k}$  may, in general, have either real or complex components and is connected with the coefficients of the difference equation by the relation  $\sum A(\underline{h})e^{i\underline{k}\cdot\underline{h}} = 0$ . But while this equation fixes  $E$  as a function of  $\underline{k}$  since  $A(\underline{h})$  is linear in  $E$ , for every value of  $E$  there are many possible values of  $\underline{k}$  and consequently many particular solutions. The general solution is a linear combination of the particular solutions. By using the boundary conditions we can determine the allowed values of  $\underline{k}$  and of  $E$ , and the coefficients in the linear combination.

To make this method clear, let us consider the case of a  $G$  by  $G$  lattice in which only the interactions of an atom with its four nearest neighbors are important. If the wave functions represent atoms in an  $s$  state, the difference equation becomes

$$\alpha c_{\underline{g}_1, \underline{g}_2} + c_{\underline{g}_1+1, \underline{g}_2} + c_{\underline{g}_1-1, \underline{g}_2} + c_{\underline{g}_1, \underline{g}_2+1} + c_{\underline{g}_1, \underline{g}_2-1} = 0 \quad (35)$$

where  $\alpha = A(\underline{0})/A(\underline{1})$ . For boundary conditions at the side of the square we take the equations

$$\begin{aligned} \alpha c_{\underline{g}_1, 1} + c_{\underline{g}_1+1, 1} + c_{\underline{g}_1-1, 1} + c_{\underline{g}_1, 2} &= 0 \\ \alpha c_{\underline{g}_1, G} + c_{\underline{g}_1+1, G} + c_{\underline{g}_1-1, G} + c_{\underline{g}_1, G-1} &= 0 \\ \alpha c_{1, \underline{g}_2} + c_{2, \underline{g}_2} + c_{1, \underline{g}_2+1} + c_{1, \underline{g}_2-1} &= 0 \\ \alpha c_{G, \underline{g}_2} + c_{G-1, \underline{g}_2} + c_{G, \underline{g}_2+1} + c_{G, \underline{g}_2-1} &= 0, \end{aligned} \quad (36)$$

while at the corners we take

$$\begin{aligned} \alpha c_{1,1} + c_{2,1} + c_{1,2} &= 0 & \alpha c_{G,1} + c_{G-1,1} + c_{G,2} &= 0 \\ \alpha c_{1,G} + c_{2,G} + c_{1,G-1} &= 0 & \alpha c_{G,G} + c_{G-1,G} + c_{G,G-1} &= 0. \end{aligned} \quad (37)$$

These equations are convenient mathematically since now the problem is equivalent to the problem of the two-dimensional analogue of the loaded string; but they are not quite right physically. They would give the boundary conditions developed on page 38 if  $\alpha$  were replaced by  $\alpha - V_0/4A(\underline{1})$  in (36) and by  $\alpha - V_0/2A(\underline{1})$  in (37). Substituting  $c_{\underline{g}} = e^{i\underline{g} \cdot \underline{k}}$  in (35) gives  $\alpha + 2\cos k_1 + 2\cos k_2 = 0$ . Since changing the sign of  $k_1$  or of  $k_2$  does not affect  $\alpha$ , we try letting  $c_{\underline{g}} = C_1 e^{i(g_1 k_1 + g_2 k_2)} + C_2 e^{i(g_1 k_1 - g_2 k_2)} + C_3 e^{-i(g_1 k_1 + g_2 k_2)} + C_4 e^{-i(g_1 k_1 - g_2 k_2)}$ . We find that this combination contains enough terms to enable us to satisfy (36) and (37). The boundary conditions require that  $k_1$  and  $k_2$  take only the values  $f\pi/(G+1)$  where  $f$  is any integer between 1 and  $G$ , inclusive, and that the  $C$ 's be such that  $c_{\underline{g}} = C \sin(g_1 k_1) \sin(g_2 k_2) = C \sin(\pi f_1 g_1 / (G+1)) \sin(\pi f_2 g_2 / (G+1))$ . Comparison of this result with that for cyclic boundary conditions shows that the change in boundary conditions has made but an insignificant change in the energy spectrum. We therefore can hope that it is not necessary to use the accurate boundary conditions and that we can use any conditions that are mathematically convenient and that resemble the true conditions fairly closely.

§10. Attempted Solutions in a Magnetic Field

Having considered the various methods by which solutions of

$$\sum_{\underline{h}} \exp[iB(\underline{g}_1 h_2 - \underline{g}_2 h_1)] \underline{A}(\underline{g}-\underline{h}) c_{\underline{h}} = 0 \quad (28)$$

can be obtained when  $H = 0$ , let us now consider the problem when a magnetic field is present. Since there are no obvious solutions to be obtained by inspection, we turn at once to the matrix method.

A particularly simple matrix results if we consider a  $G$  by  $G$  lattice in which we assume that only the interactions of an atom with its four nearest neighbors matter, that the wave functions represent atoms in an  $s$  state, and that the boundary conditions are the mathematically convenient ones that reduce to (36) and (37) when there is no magnetic field. These conditions are evident from the form of the matrix which is

$$A = \begin{vmatrix} B_1 & D^+ & 0 & \dots & 0 & 0 \\ D^- & B_2 & D^+ & \dots & 0 & 0 \\ 0 & D^- & B_3 & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & B_{G-1} & D^+ \\ 0 & 0 & 0 & \dots & D^- & B_G \end{vmatrix} \quad \text{where } B_m = \begin{vmatrix} \alpha & \beta^m & 0 & \dots & 0 & 0 \\ \beta^{-m} & \alpha & \beta^m & \dots & 0 & 0 \\ 0 & \beta^{-m} & \alpha & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & \alpha & \beta^m \\ 0 & 0 & 0 & \dots & \beta^{-m} & \alpha \end{vmatrix} \quad \text{and} \quad (38)$$

$$D = \begin{vmatrix} B & 0 & 0 & \dots & 0 & 0 \\ 0 & B^2 & 0 & \dots & 0 & 0 \\ 0 & 0 & B^3 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & B^{G-1} & 0 \\ 0 & 0 & 0 & \dots & 0 & B^G \end{vmatrix}$$

We have divided (28) through by  $A(\underline{1})$  so that  $a = A(\underline{0})/A(\underline{1})$  and  $B = e^{iB}$ .

Frequently an infinite lattice is more convenient to work with than a finite one. The most obvious thing to do in such a case is to set up some kind of "cyclic" boundary conditions so that we have only a finite number of equations to work with. The simplest boundary condition would be to require that  $c_{\underline{h}+\underline{f}G} = c_{\underline{h}}$ . (28) then becomes

$$\sum_{\underline{h}} \sum_{\underline{f}}^G \exp[iB(\underline{g}_1 \underline{h}_2 - \underline{g}_2 \underline{h}_1 + \underline{g}_1 \underline{f}_2 G - \underline{g}_2 \underline{f}_1 G)] A(\underline{g} - \underline{h} - \underline{f}G) = 0 \quad (28')$$

If we let  $\underline{g}$  run over the  $G^2$  values defined by  $1 \leq \underline{g}_1, \underline{g}_2 \leq G$ , we appear to get the desired set of  $G^2$  simultaneous, homogeneous equations in  $G^2$  unknowns. However, there is no justification for limiting  $\underline{g}$  in this manner; we must let its components take on all integral values. When we do this, the resulting infinite set of equations in  $G^2$  unknowns is inconsistent.

To show that the equations of this set are inconsistent, consider the subset obtained when  $\underline{g} = \underline{g}' + \underline{n}G$  and  $\underline{f} = \underline{f}' + \underline{n}$  in (28') where  $\underline{g}'$  is fixed and chosen so that  $A(\underline{g}' - \underline{h} - \underline{f}'G) = 0$  unless  $\underline{f}' = 0$ . If  $\underline{n} = (n_1, n_2)$  is chosen so that  $n_2 = 0$  while  $n_1$  may be either -1, 0, or +1 we get



$$\begin{aligned} & \frac{G}{h} e^{iB(g_1' h_2 + n_1 h_2 - g_2' h_1)} A(g' - h) \\ &= \sum_{h_2} \frac{G}{h_2} e^{iB n_1 h_2} \left[ \sum_{h_1} \frac{G}{h_1} e^{iB(g_1' h_2 - g_2' h_1)} A(g' - h) \right] \\ &= \sum_{h_2} \frac{G}{h_2} e^{iB n_1 h_2} E(h_2; g') = 0. \end{aligned}$$

In the cases in which we are interested  $A(g' - h) = 0$  unless  $h_2$  is either  $g_2' - 1$ ,  $g_2'$ , or  $g_2' + 1$ . Therefore

$$\begin{aligned} & e^{iB n_1 (g_2' - 1)} E(g_2' - 1; g') + e^{iB n_1 g_2'} E(g_2'; g') \\ &+ e^{iB n_1 (g_2' + 1)} E(g_2' + 1; g') = 0, \quad n_1 = -1, 0, 1. \end{aligned}$$

The condition that these three simultaneous equations in three unknowns, the E's, be consistent is that

$$\begin{vmatrix} e^{-iB(g_2' - 1)} & e^{-iB g_2'} & e^{-iB(g_2' + 1)} \\ 1 & 1 & 1 \\ e^{+iB(g_2' - 1)} & e^{+iB g_2'} & e^{+iB(g_2' + 1)} \end{vmatrix} = 0.$$

This requires that  $e^{2iB} - 2e^{iB} + 2e^{-iB} - e^{-2iB} = 0$  or  $e^{-2iB} (e^{iB} - 1)^3 (e^{iB} + 1) = 0$ . Since  $B \ll 1$  for all values of the magnetic field in which we are interested, this expression can not equal zero and we have shown that three of the equations of the infinite set are inconsistent.

Let us attempt, by properly choosing  $c_{\underline{h}}$ , to reduce the infinite number of equations that result from (28) when we have to do with an infinite lattice to the set of  $G^2$  equations that we get when  $1 \leq g_1, g_2 \leq G$ . To do this we can always write  $c_{\underline{h}+\underline{f}G} = F(\underline{f}, \underline{h})c_{\underline{h}}$  so that (28) will become

$$\sum_{\underline{h}}^G c_{\underline{h}} \sum_{\underline{f}}^{\infty} e^{iB[g_1 h_2 - g_2 h_1 + G(g_1 f_2 - g_2 f_1)]} F(\underline{f}, \underline{h}) A(\underline{g} - \underline{h} - \underline{f}G) = 0. \quad \text{Consider}$$

the set of equations obtained when  $\underline{f}$  is replaced by  $\underline{f} + \underline{n}$  and  $\underline{g} = \underline{g}' + \underline{n}G$  where  $\underline{g}'$  is fixed and the components of  $\underline{n}$  take on all integral values. It is

$$\sum_{\underline{h}}^G c_{\underline{h}} \sum_{\underline{f}}^{\infty} e^{iB[g_1' h_2 - g_2' h_1 + G(n_1 h_2 - n_2 h_1 + g_1' f_2 - g_2' f_1 + g_1' n_2 - g_2' n_1) + G^2(n_1 f_2 - n_2 f_1)]} \times$$

$$\times F(\underline{f} + \underline{n}, \underline{h}) A(\underline{g}' - \underline{h} - \underline{f}G) = 0 \quad (39)$$

For most  $\underline{g}'$ ,  $A(\underline{g}' - \underline{h} - \underline{f}G) = 0$  unless  $\underline{f} = 0$  so that

$$\sum_{\underline{h}}^G c_{\underline{h}} e^{iB[g_1' h_2 - g_2' h_1 + G(n_1 n_2 - n_2 n_1)]} F(\underline{n}, \underline{h}) A(\underline{g}' - \underline{h}) = 0 \quad (40)$$

A sufficient condition that these equations be true for all  $\underline{n}$  is evidently that  $F(\underline{n}, \underline{h}) = e^{-iBG(n_1 h_2 - n_2 h_1)}$ . Since this expression for  $F$  reduces all the equations of (40) to the same equation, it introduces no restrictions on the energy. Hence while we have not proved that it is necessary to choose  $F$  thus, it would appear that any other choice would produce a

set of simultaneous equations to be solved and that troublesome restrictions on the possible values of the  $c_{\underline{h}}$ 's and the  $A(\underline{h})$ 's would be introduced. If we consider those values of  $\underline{g}$ ' that correspond to atoms on the boundary of the region defined by  $1 \leq g_1, g_2 \leq G$ , we find that  $\underline{f}$  is not limited to one value and that we must consequently require that the magnetic field,  $H$ , be such that  $BG^2 = 2\pi N$ , where  $N$  is an integer.

This restriction must be introduced to eliminate the term in  $G^2$  in the exponential in (39). If we wish to have  $H = 1000$  N gauss, this means that  $G$  must be about 600. Hence for reasonably large crystals the only serious restriction on  $H$  is that it not vary continuously.

Let us consider the effect of the conditions  $c_{\underline{h}+\underline{f}G} = e^{-iBG(f_1h_2-f_2h_1)} c_{\underline{h}}$  and  $BG^2 = 2\pi N$  on the wave function of an electron in the lattice. If we compare  $\Psi(\underline{r}) = \sum_{\underline{h}} c_{\underline{h}} \psi_{\underline{h}}^0(\underline{r})$  and  $\Psi(\underline{r}+\underline{n}G\mathbf{a})$ , we find that because of the two conditions,  $\Psi(\underline{r}+\underline{n}G\mathbf{a}) = e^{iBG(xn_2-yn_1)/a} \Psi(\underline{r})$ . This means that the physical state at  $\underline{r}+\underline{n}G\mathbf{a}$  is the same as at  $\underline{r}$ , the wave functions being connected by the gauge transformation appropriate to the magnetic field that is present. These two conditions give cyclic boundary conditions in a three-dimensional cubic lattice as well as in a two-dimensional square lattice.

The necessity for restricting the magnetic field by requiring that  $BG^2 = 2\pi N$  when we want a cyclic physical situation is not peculiar to the tight binding approximation but is

present in all cases. For if  $\Psi(\underline{r})$  is any wave function in a crystal lattice, we may try to secure a cyclic physical condition by requiring that

$$\Psi(\underline{r} + n\underline{aG}) = e^{iBG(xn_2 - yn_1)/a} \Psi(\underline{r}). \quad (41)$$

It follows from

$$\Psi(0 + n_1 aG, y + n_2 aG) = \Psi(aG + [n_1 - 1]aG, y + n_2 aG) \quad (42)$$

and (41) that  $\Psi(0, y) = e^{iBG^2 n_2} e^{iBGy/a} \Psi(aG, y)$ . This can be true for all  $n_2$  only if  $BG^2 = 2\pi N$ . It may be objected that (42) does not hold as an identity since in order to define  $\Psi$  uniquely and consistently in such a way that (41) is satisfied, we must restrict  $\underline{r}$  in (41) so that its components lie between 0 and  $aG$ . However, (42) still holds since  $\Psi$  must be continuous. Hence a necessary condition for a cyclic physical state is that the magnetic field be restricted by the equation  $BG^2 = 2\pi N$ .

Although we showed above that, because of our two conditions, the physical state is cyclic, the matrix that we get is not. Our two conditions reduce (2B) to

$$\sum_{\underline{h}} \sum_{\underline{h}'} e^{iB(g_1 h_2 - g_2 h_1)} \sum_{\underline{f}} e^{iBG[(g_1 + h_1)f_2 - (g_2 + h_2)f_1]} A(\underline{g} - \underline{h} - \underline{f}G) = 0.$$

If we work with the case in which only the interactions of an atom with its four nearest neighbors matter and in which the wave functions are spherically symmetric, then the matrix of this set of equations is

$$A = \begin{vmatrix} B & D & 0 & \dots & 0 & D_1 \\ D & B_2 & D & \dots & 0 & 0 \\ 0 & D & B_3 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & B_{G-1} & D \\ D_1 & 0 & 0 & \dots & D & B_G \end{vmatrix}, \text{ where } B_n = \begin{vmatrix} \alpha & B & 0 & \dots & 0 & B^{-n(G+1)} \\ B^{-n} & \alpha & B^n & \dots & 0 & 0 \\ 0 & B^{-n} & \alpha & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & \alpha & B^n \\ B^{n(G+1)} & 0 & 0 & \dots & B^{-n} & \alpha \end{vmatrix} \quad (43)$$

D is the diagonal matrix whose nth row and column contains the term  $B^n$ , and  $D_1$  is the diagonal matrix whose nth row and column contain the term  $B^{n(G+1)}$ . As usual,  $\alpha = A(0)/A(i)$  and  $B = e^{iB}$ .

In equations (38) and (43) we have obtained the matrices that correspond to two different sets of boundary conditions. All that remains to be done is to find the transformations that reduce these matrices to diagonal form, or, at least, to find the values of  $\alpha$  for which the determinants of the matrices are zero. Unfortunately, it is impossible to solve the problem in two stages as we did when  $H=0$  by first transforming our matrix to one in which the only non-zero terms were in  $G$  by  $G$  blocks along the diagonal. This is best seen by considering the particular cases in which  $G$  is two and three. To solve the problem in one stage seems equivalent to solving the problem by inspection.

There remains the solution by means of difference equations. In a magnetic field, (35) becomes

$$\begin{aligned} & \alpha c_{g_1, g_2} + \exp[-iBg_2] c_{g_1+1, g_2} + \exp[iBg_2] c_{g_1-1, g_2} \\ & + \exp[iBg_1] c_{g_1, g_2+1} + \exp[-iBg_1] c_{g_1, g_2-1} = 0. \end{aligned} \quad (44)$$

Satisfactory boundary conditions can easily be obtained from the matrices of (38) or (43). When there was no magnetic field this <sup>problem</sup> could be solved by what was essentially a separation of variables. We divided  $c_{\underline{g}}$  into two factors, one of which depended on  $g_1$  only and the other of which depended on  $g_2$  only. It is not possible to do this with (44). While it will consequently be difficult to solve (44), still the difference equation method seems the most promising for future work since there are several powerful methods of attack.

### §11. Solutions for a Two by Two Lattice and the Calculation of the Magnetic Susceptibility

Since we have thus far been unable to solve any general case, let us consider the case of a 2x2 lattice and attempt to get some indication of the magnetic susceptibility of the general lattice from the easily calculable susceptibility of this simple system. When  $G$  is two, the matrix (38) becomes

$$A = \begin{vmatrix} \alpha & \beta & \beta^{-1} & 0 \\ \beta^{-1} & \alpha & 0 & \beta^{-2} \\ \beta & 0 & \alpha & \beta^2 \\ 0 & \beta^2 & \beta^{-2} & \alpha \end{vmatrix}$$

Since we have only four equations in four unknowns, we can solve by elementary algebra. We find the four solutions to be

$$\begin{aligned}
 \alpha_1 &= -2\cos B/2, & c_{1,1}:c_{1,2}:c_{2,1}:c_{2,2} &= 1: \beta^{-3/2} : \beta^{3/2} : 1; \\
 \alpha_2 &= -2\sin B/2, & &= 1: i\beta^{-3/2} : -i\beta^{3/2} : -1; \\
 \alpha_3 &= 2\sin B/2, & &= 1:-i\beta^{-3/2} : i\beta^{3/2} : -1; \\
 \alpha_4 &= 2\cos B/2, & &= 1:-\beta^{-3/2} : -\beta^{3/2} : 1.
 \end{aligned} \tag{45}$$

From these solutions of the matrix, we will determine the values of the energy. In (38) we chose our boundary conditions so that the matrix would have a mathematically simple form but disregarded the physical meaning of the conditions. Since all the atoms are corner atoms in a 2x2 crystal, we get this same matrix and the same set of solutions if we use the physically proper boundary conditions developed on page 38 provided we redefine  $\alpha$  to be

$$\alpha = [A(0) - V_0/2] / A(1)$$

From (29) it follows that

$$\alpha_n = [E^0 - E_n + R_0 + V_0/2] / [(E^0 - E_n)\Delta_1 + V_1 + R_1]$$

If we solve this for  $E_n$  and expand the denominator of the resulting expression by means of the binomial theorem, we get

$$E_n = E^0 + V_0/2 + R_0 + \alpha_n(-V_1 - R_1 + \Delta_1 V_0/2 + \Delta_1 R_0) - \alpha_n^2 \Delta_1 (V_1 + R_1)$$

where  $n=1,2,3$ , or 4. When there is no magnetic field,  $\alpha_2 = \alpha_3$  so that half of the levels are degenerate. The presence of the field removes the degeneracy.

To get numerical expressions for the characteristic energies we will expand  $\alpha_n$  in a power series in B and will use (33) which means that we consider a crystal whose lattice constant is  $6a_0$ . This gives

$$\begin{aligned}
 E_1 &= [E^0 + V_0 / 2 + R_0] - .2 \times 10^{-14} - 7.8 \times 10^{-31} H^2 \text{ ergs,} \\
 E_2 &= [E^0 + V_0 / 2 + R_0] - 5.49 \times 10^{-22} H + 2.06 \times 10^{-30} H^2 \text{ ergs,} \\
 E_3 &= [E^0 + V_0 / 2 + R_0] + 5.49 \times 10^{-22} H + 2.06 \times 10^{-30} H^2 \text{ ergs,} \\
 E_4 &= [E^0 + V_0 / 2 + R_0] + 28.7 \times 10^{-14} - 4.34 \times 10^{-30} H^2 \text{ ergs.}
 \end{aligned}
 \tag{46}$$

The common term,  $E^0 + V_0 / 2 + R_0 = -3.63 \times 10^{-11} + 1.96 \times 10^{-30} H^2$ , is treated separately since we will be interested in the distance between the levels. These distances are to be compared with  $kT$  which, if  $T=300$ , is  $4.14 \times 10^{-14}$  ergs. It is evident that at all ordinary magnetic field strengths the first three levels will differ by much less than  $kT$  while  $E_4$  will be higher by  $7kT$  than any of the others. Investigation of this close grouping of the lower three levels show us that it is due to the fact that the first numerical term in  $E_1$  is the difference of two terms that are nearly equal. It is for this reason that we can calculate the value of this term to but one significant figure. Further investigation shows that the first numerical term in  $E_1$  is very sensitive to  $\rho$ , the relative distance between the atoms of our lattice. This is shown in the following tabulation:



$$\begin{aligned} \rho &= 5.8, 5.9, 5.99, 6.0, 6.3, \\ [E_2 - E_1] \times 10^{14} &= -4.0, -2.3, -.001, .2, 4.8. \end{aligned} \quad (47)$$

To complete our picture of the distribution of energy levels we must note that each of the four levels is split into two levels because of the spin of the electrons; that is, we must add to  $E_n$  the term  $\pm (e\hbar H)/(2mc) = \pm 9.28 \times 10^{-21} H$ .

From these expressions for the energy we can readily calculate the magnetic susceptibility. The magnetic moments associated with the states are

$$\begin{aligned} m_1 &= - \partial E_1 / \partial H = 1.56 \times 10^{-30} H \text{ e.m.u.}, \\ m_2 &= - \partial E_2 / \partial H = 5.49 \times 10^{-22} - 4.12 \times 10^{-30} H \text{ e.m.u.}, \\ m_3 &= - \partial E_3 / \partial H = -5.49 \times 10^{-22} - 4.12 \times 10^{-30} H \text{ e.m.u.}, \\ m_4 &= - \partial E_4 / \partial H = 8.68 \times 10^{-30} H \text{ e.m.u.} \end{aligned} \quad (48)$$

Since we are principally interested in the effects produced by the lattice, we have omitted from these expressions the contribution to the magnetic moment that results from  $R_0$ . This contribution, which is just the magnetic moment of the free atom, deducts  $3.92 \times 10^{-30} H$  e.m.u. from the moment of each of the states of (47) and produces a diamagnetic term,  $\chi_{\text{mol}} = -2.36 \times 10^{-6}$ , in the molar susceptibility. We will also, as is usual, consider separately the spin paramagnetism of the electrons. This arises from the magnetic moment,  $\mp 9.28 \times 10^{-21}$ , associated with the spin that must be added to each of the states of (48).

If the temperature were high enough so that the electrons were uniformly distributed over the various energy levels, or if there were no spin so that there were only four states for the four electrons, each of the states of (46) would be occupied by one electron. Since the magnetic moment of the system is the sum of the magnetic moments associated with the various states, it would be  $2.12 \times 10^{-30} \text{H e.m.u.}$  The quantity that is usually computed is the molar susceptibility  $\chi_{\text{mol}}$ . For our  $2 \times 2$  crystal the molar susceptibility is equal to the magnetic moment of the crystal times Avogadro's number divided by four H. This gives  $\chi_{\text{mol}} = 3.19 \times 10^{-7}$  as the contribution of the effects produced by the lattice to the molar susceptibility in this particular case in which we consider, effectively, only the terms in  $H^2$  and in which we weight the various levels equally.

Another case that should be considered is the usual one in which each of the levels of (46) can accommodate two electrons, other effects of spin being neglected. The distribution of electrons is obtained from the Fermi function, the average number of electrons in a state being  $\frac{2}{e^{\alpha + \beta E} + 1}$  where  $\alpha$  is determined by equating the sum of the probabilities to four, the number of electrons in the system, and  $\beta$  is  $1/kT$ . Consideration of (46) and (47) shows us that by slightly varying the lattice constant and by changing the temperature we can get any of a wide variety of distributions. Very

high temperatures give the results of the last paragraph. If the lattice constant is  $5.99 a_0$ , we find that the average number of electrons in each of the first three states is the same and that there is only about one chance in a thousand of finding an electron in the fourth state. Under these circumstances the terms containing  $H$  in (48) contribute to the molar susceptibility the term  $\chi_{\text{mol}} = - 1.34 \times 10^{-6}$ . If the lattice constant is changed somewhat, say to  $6a_0$ , the susceptibility will be of this order of magnitude but we may get any of a considerable range of values and may get a peculiar temperature dependence for the susceptibility. Since we are interested not in the detailed properties of the  $2 \times 2$  lattice but only in general properties that may give us a little insight into the properties of a  $G \times G$  lattice, it does not seem worthwhile to make detailed calculations of the molar susceptibility in various cases. The general properties that seem to be worth noting are that we get a molar susceptibility of the order of magnitude of  $10^{-6}$ , that the precise magnitude seems to be very sensitive to the lattice constant, that the susceptibility may not be independent of temperature, and that while the sign tends to be negative, it can be positive under some circumstances. A consideration of Van Vleck [16], p.187, shows that the temperature dependence should drop out in the general case since the distance between energy levels will be much smaller than in the  $2 \times 2$  lattice. There seems to be no evident reason why the other general properties of the  $2 \times 2$  lattice

could not be properties of the general lattice.

In the above discussion we have neglected those terms in (48) that are independent of the field. This cannot be done for a 2x2 lattice since these terms give rise to a temperature dependent, paramagnetic term in the molar susceptibility whose order of magnitude is  $10^{-4}/T$ . While this is large, a much larger corresponding term would result if  $\mp 9.28 \times 10^{-21}$ , the magnetic moment due to the spin, were added to each of the magnetic moments of (48). Since we know that, in a system having many energy levels, Fermi-Dirac statistics shows that the spin contributes only a relatively small, temperature independent, paramagnetic term to the susceptibility, we may conclude that in a large lattice the terms in (48) that are independent of H will produce a much smaller effect and may be neglected.

Our results, that the molar susceptibility due to the lattice structure is of the order of  $10^{-6}$ , that its precise magnitude is very sensitive to the lattice constant, that its sign might be positive, and that it is probably independent of temperature in the general case, may be compared with susceptibilities determined from other models. If the atoms of our lattice are separated far enough so that they can be considered as isolated atoms, their molar susceptibility is independent of T, being  $-2.36 \times 10^{-6}$ . Landau [10] found that the susceptibility of free electrons was

independent of  $T$ , being  $-3 \times 10^{-6}$  for lithium. Peierls [12] has developed a method for calculating the susceptibilities of electrons in a crystal lattice without determining the characteristic energies. While it seems to be difficult to get numerical results by his method, it can be seen that his molar susceptibilities are of the same order of magnitude as the others that we have been considering and that their sign depends in a complicated way on the lattice structure.

It should be noted that we have not made the usual assumption that  $\Delta_1 = 0$ . Although  $\Delta_1$  is only about  $1/20$  for the value of  $\rho$  that we have used, while  $\Delta_0$  is 1,  $\Delta_1$  is practically as important as  $\Delta_0$  in calculating the susceptibility.

## FLOQUET'S THEOREM IN A MAGNETIC FIELD

### §12. Introduction

One of the most convenient methods for solving the set of simultaneous equations that arises in the tightly bound electron approximation when there is no magnetic field is that given by Fröhlich [5], p. 30. This method depends on the theorem that the energy characteristic wave functions that represent the state of an electron in a periodic potential can be put in the form  $\psi_{\underline{k}}(\underline{r}) = e^{i\underline{k} \cdot \underline{r}} u_{\underline{k}}(\underline{r})$  where  $u_{\underline{k}}(\underline{r})$  has the same periodicity as the potential. We will call this theorem Floquet's theorem although Floquet considered only the one-dimensional case, leaving to Bloch [3] the development of the three-dimensional analogue. If we could develop

a theorem of this kind that was valid in a magnetic field, we ought to be able to complete our solution of the tightly bound electron approximation in a magnetic field. Furthermore, since Floquet's theorem is fundamental to most of the wave mechanical treatment of the theory of metals, we must develop an analogue of Floquet's theorem that is valid in a magnetic field if we wish to work with states that are exact in a magnetic field. Floquet's theorem is fundamental since degenerate states are usually most easily treated when they are classified as indicated by the theorem. The specification of  $\underline{k}$  provides the notation in terms of which the state of an electron is usually described. Floquet's theorem is also used in the proof of a number of important theorems. For example, it was used by Jones and Zener [8] to obtain a general proof that the average velocity of an electron is given by  $\bar{\underline{v}} = \text{grad}_{\underline{k}} E/\hbar$ . This equation is prominent in all discussions of conductivity. The important method of treatment invented by Wigner and Seitz [17] and particularly its extension by Slater [13] are usually developed from Floquet's theorem. It is, therefore, very important to determine whether or not Floquet's theorem still holds when we investigate the wave functions of an electron in a periodic lattice potential and a uniform magnetic field.

In §12 we give the proof of Floquet's theorem when there is no magnetic field and in §13 we consider the effect of the field. We find that the field causes the usual proof

to break down and our investigations indicate that if some analogue of Floquet's theorem is valid in a magnetic field, its form is not one of those that we consider. The best that we can do is to obtain a two-dimensional analogue, one dimension coinciding in direction with the magnetic field. This analogue is of very little use. We also find that the Wigner-Seitz method and Slater's method do not seem to be applicable to the determination of exact wave functions in a magnetic field.

### §13. Proof of Floquet's Theorem in the Absence of a Field

First consider the proof, as given by Wilson [18] p. 37, of Floquet's theorem when there is no magnetic field. We will deal with a Bravais lattice in which the positions of the lattice points are given by  $g_1 \underline{a}_1 + g_2 \underline{a}_2 + g_3 \underline{a}_3$ , where  $\underline{a}_1, \underline{a}_2, \underline{a}_3$  are the axes of the lattice and  $g_1, g_2, g_3$  are integers. The periodicity of the potential is expressed by the equation  $V(\underline{r}) = V(\underline{r} + \underline{a}_1 g_1 + \underline{a}_2 g_2 + \underline{a}_3 g_3)$ . Consider the set of linearly independent, degenerate, wave functions having the energy  $E$ ,

$$\psi_1(\underline{r}, E), \psi_2(\underline{r}, E), \dots, \psi_n(\underline{r}, E)$$

Since  $\psi_t(\underline{r} + \underline{a}_1, E)$  is a solution of Schrödinger's equation with the same energy as the members of the set, it must be expressible as a linear combination of these functions. Therefore

$$\psi_t(\underline{r}+\underline{a}_1, E) = \sum_{s=1}^n p_{st}^{(1)} \psi_s(\underline{r}, E).$$

Likewise

$$\psi_t(\underline{r}+\underline{a}_2, E) = \sum_{s=1}^n p_{st}^{(2)} \psi_s(\underline{r}, E),$$

$$\psi_t(\underline{r}+\underline{a}_3, E) = \sum_{s=1}^n p_{st}^{(3)} \psi_s(\underline{r}, E)$$

where  $p_{st}^{(j)}$  is an element of the matrix  $P^{(j)}$ .

Since the displacement operators to which the matrices  $P^{(1)}$ ,  $P^{(2)}$ , and  $P^{(3)}$  correspond commute, the matrices all commute. Consequently they can simultaneously be reduced to diagonal form by means of a canonical transformation

$$\psi_t' = \sum_{s=1}^n T_{st} \psi_s. \quad \text{This gives}$$

$$\psi_t'(\underline{r}+\underline{a}_j, E) = \exp(ik_j a_j) \psi_t'(\underline{r}, E)$$

where  $j = 1, 2, 3$ . It follows that the members of the primed set are of the form

$$\psi_{\underline{k}}'(\underline{r}) = e^{i\underline{k} \cdot \underline{r}} u_{\underline{k}}(\underline{r}) \quad (49)$$

where  $u_{\underline{k}}(\underline{r})$  has the same periodicity as the potential and where  $\underline{k} = (k_1, k_2, k_3)$  can now be used instead of the subscript  $t$  to designate the different members of the set. We have shown that any wave function can be represented as the sum of wave functions of the form of (49); hence it is customary to take this set as the fundamental set.



§14. Effect of a Magnetic Field

A magnetic field introduces complications because of the fact that if  $\psi(\underline{r})$  is an energy characteristic solution of Schrödinger's equation for a periodic potential  $\psi(\underline{r}+\underline{a})$  is not a solution. Instead, when the scalar potential  $V(\underline{r})$  is periodic with period  $\underline{a}$  and the vector potential,  $\underline{A}=(-Hy/2, Hx/2, 0)$ , is that corresponding to a uniform magnetic field in the z-direction, then if  $\psi(\underline{r})$  is an energy characteristic solution of Schrödinger's equation with energy, E,

$$\psi(\underline{r}+\underline{a}) \exp[-ie(\underline{r}\underline{x}\underline{a}) \cdot \underline{H}/2c\hbar] \quad (50)$$

is also a solution having the same energy. If we are dealing with a Bravais lattice so that  $V(\underline{r})$  is triply periodic with periods  $\underline{a}_1$ ,  $\underline{a}_2$ , and  $\underline{a}_3$ , then (50) can be applied to each period.

Let us attach subscripts to the axes of our Bravais lattice in such a way that neither  $\underline{a}_1$  nor  $\underline{a}_2$  is parallel to the magnetic field. Consequently  $(\underline{a}_1 \underline{x} \underline{a}_2) \cdot \underline{H} \neq 0$ . It follows from (50) that

$$\psi_t(\underline{r}+\underline{a}_j) \exp[-ie(\underline{r}\underline{x}\underline{a}_j) \cdot \underline{H}/2c\hbar] = \sum_s p_{st}^{(j)} \psi_s(\underline{r}) \quad (51)$$

where  $j=1,2$  and  $p_{st}^{(j)}$  is an element of the matrix  $P^{(j)}$ . Now from (51)

$$\begin{aligned} \sum_{s,t} p_{ns}^{(1)} p_{st}^{(2)} \psi_t(\underline{r}) &= \sum_s p_{ns}^{(1)} \exp[-ie(\underline{r}\underline{x}\underline{a}_2) \cdot \underline{H}/2c\hbar] \psi_s(\underline{r}+\underline{a}_2) \\ &= \exp[-ie\{(\underline{r}\underline{x}\underline{a}_2) + (\underline{r}\underline{x}\underline{a}_1) + (\underline{a}_2 \underline{x} \underline{a}_1)\} \cdot \underline{H}/2c\hbar] \psi_n(\underline{r}+\underline{a}_1+\underline{a}_2). \end{aligned}$$

Since this is not symmetrical in 1 and 2 unless  $H=0$ ,  $P^{(1)}$  and  $P^{(2)}$  do not commute. Consequently the presence of a magnetic field prevents us from simultaneously reducing  $P^{(1)}$  and  $P^{(2)}$  to diagonal form and our attempt to prove Floquet's theorem by the method used when there was no field breaks down. The best that we can do is to find two different sets of wave functions,  $\psi_t^{(1)}$  and  $\psi_t^{(2)}$  such that

$$\begin{aligned} \psi_t^{(1)}(\underline{r}+\underline{a}_1) \exp[-i\epsilon(\underline{r}\underline{x}\underline{a}_1) \cdot \underline{H}/2c\hbar] &= \exp[ik_1 a_1] \psi_t^{(1)}(\underline{r}) \\ \psi_t^{(2)}(\underline{r}+\underline{a}_2) \exp[-i\epsilon(\underline{r}\underline{x}\underline{a}_2) \cdot \underline{H}/2c\hbar] &= \exp[ik_2 a_2] \psi_t^{(2)}(\underline{r}). \end{aligned} \quad (52)$$

If  $\underline{a}_3$  is not parallel to  $\underline{H}$ , the above discussion applies and all that we can do until we can find a valid proof of Floquet's theorem is to introduce still a third set of wave functions for which an equation analogous to (52) holds. But if  $\underline{a}_3$  is parallel to  $\underline{H}$ , then  $(\underline{a}_3 \underline{x} \underline{a}_j) \cdot \underline{H} = 0$  for  $j=1,2$ , and the matrix,  $P^{(3)}$ , that gives a displacement in the  $\underline{a}_3$  direction, commutes with both  $P^{(1)}$  and  $P^{(2)}$ . Hence  $P^{(3)}$  and either one of the other two matrices may simultaneously be reduced to diagonal form. We can therefore find two different sets of functions such that for one

$$\psi_t^{(1)}(\underline{r}+g_1 \underline{a}_1 + g_3 \underline{a}_3) = e^{i(k_1 g_1 a_1 + k_3 g_3 a_3)} e^{i\epsilon(\underline{r}\underline{x}g_1 \underline{a}_1) \cdot \underline{H}/2c\hbar} \psi_t^{(1)}(\underline{r}) \quad (53)$$

while for the other

$$\psi_t^{(2)}(\underline{r} + g_2 \underline{a}_2 + g_3 \underline{a}_3) = e^{i(k_2 g_2 a_2 + k_3 g_3 a_3)} e^{i \underline{r} \cdot \underline{g}_2 \underline{a}_2 \cdot \underline{H} / 2c\hbar} \psi_t^{(2)}(\underline{r}). \quad (54)$$

If it seems desirable, these relations can be given a form more like that of (49). For the present let us restrict ourselves to the case in which  $\underline{a}_1$ ,  $\underline{a}_2$ , and  $\underline{a}_3$  are mutually perpendicular. We must introduce the discontinuous functions of  $\underline{r}$ ,  $\underline{\rho} = \gamma_1 \underline{a}_1 + \gamma_2 \underline{a}_2 + \gamma_3 \underline{a}_3$ , defined by the condition that the vector  $\underline{r} - \underline{\rho} = (x - \gamma_1 a_1, y - \gamma_2 a_2, z - \gamma_3 a_3)$  end in the unit cell of the lattice that surrounds the atom at the origin. If we let  $u_{\underline{k}}^{(1)}(\underline{r})$  be the discontinuous function of  $\underline{r}$  defined by the fact that it is doubly periodic with periods  $\underline{a}_1$  and  $\underline{a}_3$  and that  $\exp[i\underline{k} \cdot \underline{r}] u_{\underline{k}}^{(1)}(\underline{r}) = \psi_{\underline{k}}^{(1)}(\underline{r})$  in the region in which  $\gamma_2 = 0$ , then (53) becomes

$$\psi_{\underline{k}}^{(1)}(\underline{r}) = \exp[i\underline{k} \cdot \underline{r}] \exp[i \underline{r} \cdot \underline{\gamma}_1 \underline{a}_1 \cdot \underline{H} / 2c\hbar] u_{\underline{k}}^{(1)}(\underline{r}) \quad (55)$$

We have labeled our wave functions with the appropriate value of  $\underline{k}$  rather than use a separate subscript,  $t$ . In just the same way, (54) may be put in the form

$$\psi_{\underline{k}}^{(2)}(\underline{r}) = \exp[i\underline{k} \cdot \underline{r}] \exp[i \underline{r} \cdot \underline{\gamma}_2 \underline{a}_2 \cdot \underline{H} / 2c\hbar] u_{\underline{k}}^{(2)}(\underline{r}) \quad (56)$$

where  $u_{\underline{k}}^{(2)}(\underline{r})$  is doubly periodic with periods  $\underline{a}_2$  and  $\underline{a}_3$ . Equations (55) and (56) hold in non-orthogonal lattices if the corresponding non-orthogonal coordinate system is used and if the vector and scalar products are given a suitable interpretation.

It might be objected that all that we have done is shown that this method fails to provide an analogue of Floquet's theorem when there is a magnetic field but that we have not shown that no analogue of Floquet's theorem exists. However, it seems reasonably clear that if there is to be any analogue of Floquet's theorem whose form is at all like the forms that we have been considering, it must try to combine (53) and (54), suppressing the superscripts on the  $\psi$ 's. But (53) and (54) are inconsistent as may readily be seen by using them in succession to calculate  $\psi(\underline{r} + \underline{a}_1 + \underline{a}_2)$  and noticing that the result depends on the order. If we try to combine (55) and (56), we might assume that

$\psi(\underline{r}) = \exp[i\mathbf{k} \cdot \underline{r}] \exp[i\mathbf{e}(\underline{r} \times \underline{p}) \cdot \underline{H} / 2c\hbar] u(\underline{r})$  where  $u(\underline{r})$  is triply periodic with periods  $\underline{a}_1$ ,  $\underline{a}_2$ , and  $\underline{a}_3$ . But if this were true, it would follow that

$$\psi(\underline{r} + \underline{a}_1) = \exp[i\mathbf{k}_1 \cdot \underline{a}_1] \exp[i\mathbf{e}(\underline{r} \times \underline{a}_1) \cdot \underline{H} / 2c\hbar] \exp[i\mathbf{e}(\underline{a}_1 \times \underline{p}) \cdot \underline{H} / 2c\hbar] \psi(\underline{r}).$$

This implies that  $\psi(\underline{r})$  is discontinuous since  $\exp[i\mathbf{e}(\underline{a}_1 \times \underline{p}) \cdot \underline{H} / 2c\hbar]$  varies discontinuously with  $\underline{r}$ . We conclude that if there is any analogue of Floquet's theorem that holds in a magnetic field it does not have either of the forms that we have been considering and it cannot be derived by the method we attempted to use.

Since we do not have a proof of Floquet's theorem that holds in a magnetic field, we cannot use the theorem

nor can we use any formula that was derived from it to give a rigorous treatment of a crystal lattice in a magnetic field. We cannot use the wave vector  $\underline{k}$  to classify the wave functions; we cannot use the formula  $\underline{v} = \text{grad}_{\underline{k}} E/\hbar$  to calculate the current; and we cannot use Fröhlich's method for determining the coefficients in the infinite series that arises in the tight-binding approximation. It is evident that Slater's method, which depends directly on Floquet's theorem, cannot be used to find wave functions if a magnetic field is present; but it is not so evident that the Wigner-Seitz method is inapplicable. The evident way to develop an analogue to the Wigner-Seitz method would be to require that

$$\Psi(\underline{r} + n\mathbf{a}) = e^{iB(xn_2 - yn_1)/a} \Psi(\underline{r}).$$

This is just (41) with  $G$  set equal to unity. We see that the entire argument of p. 52 can be applied here. The continuity conditions on  $\Psi$  restrict the magnetic field either to zero or to the impossibly large values that satisfy the condition  $B = 2\pi N$ . Consequently, it would seem that the Wigner-Seitz method cannot be used to get solutions that are exact in a magnetic field.

## CONCLUSIONS

### §15. Conclusions

The general theory of the Hall effect and the change of resistance in a magnetic field expresses these quantities in terms of a number of integrals over the surface of the Fermi distribution. The values of these integrals depend upon the form of the electron energy and the relaxation time as functions of the wave vector. If the free electron situation is assumed, the Hall effect has the right order of magnitude, but there is no change of resistance. This can be seen from a qualitative consideration of the effect of the fields on the distribution function. In the same way one can see how the anomalous Hall effect can arise.

The above integrals can be evaluated analytically to any desired degree of approximation, provided there is not too great a departure from spherical symmetry, if the shape of the surfaces of constant energy and the variation of relaxation time with direction are expressed in terms of spherical harmonics that have the symmetry of the lattice. The expression for the Hall coefficient is essentially the same as in the free electron case, and, when only the first two harmonics are retained, the computed change of resistance is of the right order of magnitude. However, contrary to the available observations, the ratio of the transverse to the longitudinal change of resistance shows a minimum value of about four. It seems improbable that this result could be changed in any

material way by the inclusion of higher series members, so that if the experimental results are to be taken as reliable, doubt is thrown on the usual method of treatment.

In treating the change of resistance in a magnetic field, we must use expressions that contain both cubes and first powers of the relaxation time. The general theory of the use of a relaxation time indicates that such a procedure may not be valid. To throw some light on this point we consider another problem in which several powers of the relaxation time appear. By using powers of the relaxation time and Boltzmann's equation we get a method that is easier than that of Guth and Mayerhöfer's for determining the current density at which Ohm's law starts to break down. We find that the deviation is first noticeable at current densities thirty times as great as those found by Guth and Mayerhöfer, and that the deviation is in the opposite direction. Both methods indicate that deviations only occur at current densities far higher than any that are experimentally attainable. Since this treatment can be carried through to a reasonably satisfactory conclusion, it does not indicate that the use of several powers of the relaxation time is not justified; but since there are convergence difficulties in the treatment, it does not allay our suspicions that such a procedure may be invalid.

In an attempt to work out a theory of the behavior of electrons in a periodic field of force that is exact in a magnetic field, we extend the tightly bound electron approximation to cover this case. The problem is set up, the necessary integrals are evaluated, and the problem is reduced to the solution of a set of simultaneous equations. The various methods of treatment of these simultaneous equations are discussed, but neither by matrix methods nor by difference equation methods do we succeed in solving them when a magnetic field is present. We consider only square lattices since the generalization to any three-dimensional lattice can be made just as easily as when no field is present.

The question of boundary conditions is considered in some detail. We find that we can set up cyclic boundary conditions in a cubic lattice if we require that  $\psi(\underline{r} + n\mathbf{a}\mathbf{G}) = \exp[i\mathbf{B}\mathbf{G}(x_2 - y_1)/a]\psi(\underline{r})$ . However, continuity requires that we restrict the magnetic field,  $H$ , to values that satisfy the equation  $G^2 e a^2 H / 2c\hbar = 2\pi N$  where  $a$  is the lattice constant,  $a\mathbf{G}$  is the length of the cycle,  $-e$  is the charge of the electron, and  $N$  is an integer.

In order to get some indication as to the meaning of our results, we complete the solution for a two by two lattice. We find the energy levels and the magnetic susceptibility of the crystal of four atoms. Our results, that the molar susceptibility is of the order of  $10^{-6}$ , that its precise



magnitude is very sensitive to the lattice constant, that its sign might be positive, and that it is probably independent of temperature, agree in general with Peierls results obtained by a different method.

A study of the three-dimensional analogue of Floquet's theorem in a magnetic field indicates that the usual derivation of the theorem is invalidated by the field and that if there is any analogue of Floquet's theorem that holds in a magnetic field, it is not the obvious one. Unless an analogue can be found, no method that depends on the use of a wave vector,  $\underline{k}$ , can be used in the treatment of wave functions that are exact in a magnetic field. It also appears that neither the Wigner-Seitz method nor Slater's extension of this method can be used to find wave functions that are exact in a magnetic field.

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