Theory of Galvanomagnetic Effects in Metals*

GALE FAIR
Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio 44135
AND
P. L. TAYLOR
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106
(Received 27 April 1970)

A solution to the linearized Boltzmann equation has been found that describes the galvanomagnetic properties of metals. The use of a vector mean-free-path function results in a solution for the conductivity tensor that is valid for any strength and orientation of the applied magnetic field. A discussion is given of the implementation of this theory to give a quantitative description of the galvanomagnetic properties of a metal when the Fermi surface and a model for the scattering of the conduction electrons are specified.

I. INTRODUCTION

The concept of a *relaxation time* for conduction electrons in metals has proved an invaluable aid in our understanding of many of those phenomena in which the effects of anisotropy are unimportant.[1] Galvanomagnetic effects, however, do not fall into this category, as it is well known that in a completely isotropic model the magnetoresistance vanishes.[2] A more cumbersome but versatile vehicle that allows the exploration of galvanomagnetic effects is the *vector mean free path*.[3] In this paper we develop a formalism based on this concept that allows a complete solution to be computed for the galvanomagnetic tensor for a model in which the current carried by independent Bloch electrons is governed by the Boltzmann equation. Our object is the development of a method in which a change in the magnitude or direction of the applied magnetic field does not necessitate a completely new computation. Instead, we first formulate an intermediate expression in which the magnetic field does not appear; the calculation of the conductivity tensor then follows with minimal computational effort as a function of the magnetic field and this intermediate expression.

This method has the advantage that it is no longer necessary to invoke the concept of the orbit in which a Bloch electron travels in a magnetic field. Few would dispute the power and elegance of the concept of electron orbits in any pedagogical display of the *qualitative* behavior of the conductivity tensor; *quantitative* calculations, however, are another matter. Most previous treatments of this problem[4] require integration over orbits that may extend into many Brillouin zones in a periodic-zone scheme if the direction of the magnetic field is close to a symmetry axis of the crystal and if the Fermi surface is multiply connected. The existence of a relaxation time must also be assumed.

The approach that we shall now describe avoids the need to trace orbits through large distances in $\mathbf{k}$ space, but at the expense of having to solve an integral equation in the first Brillouin zone. The principal advantage of our method, however, lies in the fact that it is applicable for all types of scattering between electron states.

In Sec. II we discuss the linearized Boltzmann equation in terms of the vector mean-free-path formalism. This discussion includes the closed-form solution for the mean free path. Section III includes a discussion of two scattering operators that appear in the formalism, and the separation of the problem into magnetic-field-dependent and -independent parts. The final result for the conductivity tensor is given in a form suitable for practical computations. The applications of group-representation theory to the symmetry properties of the scattering kernel and the scattering eigenfunctions are given in Secs. IV and V. Section VI is a discussion of the special case of a degenerate scattering kernel, a simple example of which is described in Sec. VII. Finally, four appendices treat in some detail the properties of the operators that appear in the formalism and some formal proofs of results from group-representation theory that are used in the text.

II. BOLTZMANN EQUATION

We consider here a metal of independent Bloch electrons of wave number $\mathbf{k}$, energy $\mathcal{E}_\mathbf{k}$, and group velocity $\mathbf{v}_\mathbf{k}$ in the presence of a constant uniform applied electric field $\mathbf{E}$ and magnetic field $\mathbf{H}$. For weak electric fields the probability that a given state is occupied differs from its equilibrium value $f_\mathbf{k}^0$ by an amount governed by the linearized Boltzmann equation[5]

$$(e/\hbar)[\mathbf{E}+(1/c)\mathbf{v}_\mathbf{k}\times\mathbf{H}]\cdot(\partial f_\mathbf{k}/\partial\mathbf{k})=(\partial f_\mathbf{k}/\partial t)_{\text{coll}}. \quad (1)$$

We assume the collision term in this equation to be due only to elastic scattering between Bloch states, so that the probability per unit time $Q(\mathbf{k},\mathbf{k}')$ that an electron is scattered from the occupied state $\mathbf{k}$ to the empty state $\mathbf{k}'$ of the same spin can be written as $Q(\mathbf{k},\mathbf{k}')=\mathcal{Q}(\mathbf{k},\mathbf{k}')\delta(\mathcal{E}_\mathbf{k}-\mathcal{E}_{\mathbf{k}'})$, with $\mathcal{Q}(\mathbf{k},\mathbf{k}')$ a smoothly varying function. We then introduce the vector mean free path $\mathbf{\Lambda}_\mathbf{k}$ defined by the relation

$$f_\mathbf{k}-f_\mathbf{k}^0=-e\mathbf{E}\cdot\mathbf{\Lambda}_\mathbf{k}(\partial f_\mathbf{k}^0/\partial\mathcal{E}_\mathbf{k}),$$

in terms of which Eq. (1) becomes[3]

$$\mathbf{v}_\mathbf{k}-(e/\hbar c)(\mathbf{v}_\mathbf{k}\times\mathbf{H}\cdot\nabla_\mathbf{k})\mathbf{\Lambda}_\mathbf{k}=\sum_{\mathbf{k}'}Q(\mathbf{k},\mathbf{k}')(\mathbf{\Lambda}_\mathbf{k}-\mathbf{\Lambda}_{\mathbf{k}'}). \quad (2)$$

It is also convenient to define an integral operator Q, such that for any function $\phi_{\mathbf{k}}$

$$Q\phi_{\mathbf{k}} \equiv \sum_{\mathbf{k}'} Q(\mathbf{k}, \mathbf{k}')\phi_{\mathbf{k}'}$$

and a scalar function

$$q_{\mathbf{k}} \equiv \sum_{\mathbf{k}'} Q(\mathbf{k}, \mathbf{k}').$$

Another operator of interest may then be defined in the form

$$T = (im/\hbar)(q-Q)^{-1}(\mathbf{v}_{\mathbf{k}} \cdot \hat{h} \times \nabla_{\mathbf{k}}), \tag{3}$$

where $\hat{h}$ is the unit vector in the direction of the magnetic field, so that $\mathbf{H} = H\hat{h}$. With the definition of the free-electron cyclotron frequency eH/mc as ω_c we then rewrite Eq. (2) in the concise form

$$(1-i\omega_c T)\mathbf{\Lambda}_{\mathbf{k}} = (q-Q)^{-1}\mathbf{v}_{\mathbf{k}}. \tag{4}$$

It has already been shown[6] that the function $(q-Q)^{-1}\mathbf{v}_{\mathbf{k}}$ exists for any physically meaningful form of scattering and velocity. It is demonstrated in Appendix A that, since the eigenvalues of T are all real, the operator $1-i\omega_c T$ possesses a well-defined inverse.

The electric current density $\mathbf{j}$ in a crystal of volume Ω is given by

$$\mathbf{j} = (e/\Omega)\sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}}$$
$$= -(e^2/\Omega)\sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}\mathbf{\Lambda}_{\mathbf{k}} \cdot \mathbf{E}\partial f_{\mathbf{k}}^0/\partial\mathcal{E}_{\mathbf{k}},$$

from which the galvanomagnetic tensor $\boldsymbol{\sigma}$ has elements

$$\sigma_{\mu\nu} = -(e^2/\Omega)\sum_{\mathbf{k}} v_\mu \Lambda_\nu (\partial f_{\mathbf{k}}^0/\partial\mathcal{E}_{\mathbf{k}}). \tag{5}$$

Our task is thus the solution of Eq. (4) to find $\mathbf{\Lambda}_{\mathbf{k}}$ for all directions and magnitudes of the applied magnetic field, and the substitution of these results in Eq. (5).

III. MAGNETIC SCATTERING EIGENFUNCTIONS

In an earlier paper[3] on the solution of the Boltzmann equation in the absence of magnetic fields it was found that the vector mean free path $\mathbf{\Lambda}_{\mathbf{k}}(\omega_c = 0)$ could usefully be considered as a linear combination of a certain subset of the eigenfunctions of the operator $q^{-1}Q$. An iterative technique was described that allowed a rapid evaluation of $\mathbf{\Lambda}_{\mathbf{k}}(\omega_c = 0)$. As a generalization of this technique we now expand the zero-magnetic-field mean free path in terms of the eigenfunctions of T. That is, we first define the complete set of magnetic scattering eigenfunctions $b_i(\mathbf{k})$ and corresponding real eigenvalues τ_i by the equations

$$Tb_i(\mathbf{k}) = \tau_i b_i(\mathbf{k}), \tag{6}$$

and then put

$$(q-Q)^{-1}v_\mu = \sum_i \beta_{\mu i} b_i(\mathbf{k}), \tag{7}$$

where v_μ is the μth Cartesian component of $\mathbf{v}_{\mathbf{k}}$. The coefficients depend on the direction but not on the magnitude of $\mathbf{H}$. It should be noted that, since the left-hand side of Eq. (7) is a real function, the magnetic scattering eigenfunctions occur in this expansion as pairs of terms of the form $\beta_{\mu i}b_i + \beta_{\mu i}^* b_i^*$. Here b_i^* is the eigenfunction corresponding to the eigenvalue $-\tau_i$ when $b_i(\mathbf{k})$ obeys Eq. (6). With this expansion the conductivity may be written as

$$\sigma_{\mu\nu} = -(e^2/\Omega)\sum_i [\beta_{\nu i}/(1-i\omega_c\tau_i)]$$
$$\times \sum_{\mathbf{k}} v_\mu(\mathbf{k}) b_i(\mathbf{k})(\partial f_{\mathbf{k}}^0/\partial\mathcal{E}_{\mathbf{k}}). \tag{8}$$

In the independent-electron model there is no reason to expect any rapid variation of $\mathbf{\Lambda}_{\mathbf{k}}$ at the Fermi surface. We accordingly replace the summation over $\mathbf{k}$ in Eqs. (2) and (8) by integrations in $\mathbf{k}$ space[5] and make the low-temperature approximation of replacing $\partial f_{\mathbf{k}}^0/\partial\mathcal{E}_{\mathbf{k}}$ by $-\delta(\mathcal{E}_{\mathbf{k}} - \mathcal{E}_F)$, with $\mathcal{E}_F$ the Fermi energy. We then find

$$\sigma_{\mu\nu} = 2e^2 \sum_i [\beta_{\nu i}/(1-i\omega_c\tau_i)] \int v_\mu(\mathbf{k}) b_i(\mathbf{k})\, d\xi. \tag{9}$$

The factor of 2 results from the summation over spin directions and

$$d\xi = dS/8\pi^3\hbar \mid \mathbf{v}_{\mathbf{k}} \mid,$$

where dS is an element of area of the Fermi surface.

The next stage in the calculation is the expansion of the magnetic scattering eigenfunctions b_i in terms of the eigenfunctions of the non-Hermitian operator $q^{-1}Q$. That is, we write

$$b_i(\mathbf{k}) = \sum_n \gamma_{in}(\hat{h}) a_n(\mathbf{k}), \tag{10}$$

where the complete set of functions $a_n(\mathbf{k})$ obey the equations

$$q^{-1}Qa_n(\mathbf{k}) = \alpha_n a_n(\mathbf{k}) \tag{11}$$

or, equivalently,

$$\int \mathcal{Q}(\mathbf{k}, \mathbf{k}') a_n(\mathbf{k}')\, d\xi' = \alpha_n a_n(\mathbf{k}) \int \mathcal{Q}(\mathbf{k}, \mathbf{k}')\, d\xi'.$$

It is shown in Appendix B that we may choose a normalization for the $a_n(\mathbf{k})$ such that

$$\int a_r(\mathbf{k}) q(\mathbf{k}) a_n(\mathbf{k})\, d\xi = \delta_{rn}.$$

With the aid of this relation we may substitute Eq. (10) in Eq. (6) to find

$$-(im/\hbar)\sum_n \gamma_{in}\hat{h} \cdot \int a_r(\mathbf{k})(\mathbf{v}_{\mathbf{k}} \times \nabla_{\mathbf{k}}) a_n(\mathbf{k})\, d\xi$$
$$= \tau_i(1-\alpha_r)\gamma_{ir}. \tag{12}$$

This takes on a simpler form with the definition of a new set of coefficients

$$\psi_{in} = \gamma_{in}(1-\alpha_n)^{1/2} \tag{13}$$

and the vector matrix

$$C_{rn} = -\frac{im}{\hbar[(1-\alpha_r)(1-\alpha_n)]^{1/2}} \int a_r(\mathbf{k})(\mathbf{v}_{\mathbf{k}} \times \nabla_{\mathbf{k}}) a_n(\mathbf{k})\, d\xi. \tag{14}$$

Then Eq. (12) becomes

$$\hat{h}\cdot\sum_n C_{rn}\psi_{in}=\tau_i\psi_{ir}. \tag{15}$$

Since the matrix C is Hermitian (Appendix C), the eigenvectors ψ_{in} are orthogonal, and may be normalized such that

$$\sum_n \psi_{in}^*\psi_{mn}=\delta_{im}. \tag{16}$$

This normalization of the ψ_{in} (and hence of the γ_{in}) determines the coefficients $\beta_{\mu i}$ of Eq. (7). Substitution of Eq. (10) in Eq. (7), multiplication by $a_r(\mathbf{k})(q-Q)$, and integration over the Fermi surface yield

$$\sum_i \beta_{\mu i}\gamma_{ir}(1-\alpha_r)=g_{\mu r},$$

where

$$g_{\mu r}\equiv\int v_\mu(\mathbf{k})a_r(\mathbf{k})\,d\xi. \tag{17}$$

Use of Eqs. (13) and (16) then yields

$$\beta_{\mu i}=\sum_r \gamma_{ir}^* g_{\mu r},$$

so that from Eq. (9)

$$\sigma_{\mu\nu}=2e^2\sum_i[1/(1-i\omega_c\tau_i)]\sum_{r,n} g_{\mu r}\gamma_{ir}\gamma_{in}^* g_{\nu n}. \tag{18}$$

To evaluate the conductivity tensor it is thus first necessary to solve Eq. (11) for the scattering eigenfunctions $a_n(\mathbf{k})$ and corresponding eigenvalues α_n. One then evaluates the coefficients C_{rn} and $g_{\mu r}$ defined in Eqs. (14) and (17), and solves Eq. (15) for the eigenvectors ψ_{ir} and eigenvalues τ_i. The conductivity is then known from Eq. (18).

IV. SYMMETRY PROPERTIES OF SCATTERING EIGENFUNCTIONS

This section deals with the symmetry properties of the scattering eigenfunctions, and the applications of these properties to computations based upon Eq. (18). We consider a metal whose lattice has the symmetry properties of a point group $\mathcal{G}$. This group consists of g rotations and rotatory reflections, where operation is symbolized by the operator $\mathcal{R}$. Then $\mathcal{R}$ operates upon a function of wave vector $\mathbf{k}$, and this operation is defined by

$$\mathcal{R}f(\mathbf{k})=f(R^{-1}\mathbf{k}), \tag{19}$$

where R is the 3×3-matrix representation of $\mathcal{R}$ that acts upon the triplet $(k_x, k_y, k_z)=\mathbf{k}$. Since the energy $\mathcal{E}_\mathbf{k}$ is a scalar under all operations of $\mathcal{G}$, the transformation properties of $\mathbf{k}$ and $\mathbf{v}_\mathbf{k}$ are easily obtained from the properties of $\mathcal{G}$. The symmetry properties of the scattering eigenfunctions, defined in Eq. (11), depend upon the symmetry properties of the kernel function $Q(\mathbf{k}, \mathbf{k}')$. Since the scattering, in the linearized approximation to the Boltzmann equation, is independent of the electric and magnetic field, the $Q(\mathbf{k}, \mathbf{k}')$ must reflect the symmetry of the lattice point group. The only assumption that must be made about the specific form of Q is summarized by the equation

$$Q(\mathbf{k}, \mathbf{k}')=Q(R\mathbf{k}, R\mathbf{k}') \tag{20}$$

for all $\mathbf{k}$ and $\mathbf{k}'$, and for all $\mathcal{R}\in\mathcal{G}$. This assumption does not require that $Q(\mathbf{k}, \mathbf{k}')$ be degenerate, or that it depend only upon $|\mathbf{k}-\mathbf{k}'|$. Clearly, Eq. (20) is a very weak restriction upon the form of the scattering kernel $Q(\mathbf{k}, \mathbf{k}')$. Equation (20), along with some results from the representation theory of point groups, is sufficient to determine the symmetry properties of the scattering eigenfunctions.

A useful result from group-representation theory is the existence of a complete set of orthonormal basis functions for the group. These functions, usually referred to as symmetry-adapted functions,[7] are linear combinations of spherical harmonics and transform, as in Eq. (19), according to the irreducible representations of each point group. For the cubic group this set of functions, Kubic harmonics, has long been known[8] and is tabulated. These functions are a complete set for the expansion of functions defined on an energy shell in a monovalent metal. Thus, we consider a set of functions $\{X_l^{jr}\}$ indexed by the angular momentum of the contributing spherical harmonics l, the label j of the irreducible representation of $\mathcal{G}$, and the column r of the representation. The most important point of this section is the following theorem, proved in Appendix D.

Theorem. Given a function $Q(\mathbf{k}, \mathbf{k}')$ that is invariant under all operations $\mathcal{R}$ of a group $\mathcal{G}$ [Eq. (20)], there exists the expansion

$$Q(\mathbf{k}, \mathbf{k}')=\sum_{ll'j} A_{ll'}^{\,j}\sum_r X_l^{jr}(\mathbf{k})X_{l'}^{jr}{}^*(\mathbf{k}'). \tag{21}$$

It is also shown in Appendix D that the function $q(\mathbf{k})$ is a scalar under $\mathcal{G}$. Therefore the modified scattering kernel of Appendix B, $Q(\mathbf{k}, \mathbf{k}')/[q(\mathbf{k})q(\mathbf{k}')]^{1/2}$, also possesses an expansion equivalent to Eq. (21). One important feature of this theorem is that the expansion given by Eq. (21) is not simply a replacement of Q by a degenerate kernel, although the meaning of such an approximation is clear. We shall return to this point in a later section.

The symmetry properties of the scattering eigenfunctions [either the $a_n(\mathbf{k})$ of Eq. (11) or, since $q(\mathbf{k})$ is a scalar, the $Y_n(\mathbf{k})$ of Eq. (B1)] may be obtained by making the connection between the symmetry-adapted functions, the expansion of Eq. (21), and the basis functions for a representation of the group $\mathcal{G}$. Basis functions for a given matrix representation of $\mathcal{G}$ are defined by[9]

$$\mathcal{R}y_j^r(\mathbf{k})=\sum_{r'} y_j^{r'}(\mathbf{k})D_{rr'}^{(j)}(R), \tag{22}$$

where $D^{(j)}(R)$ is the matrix of the group operator $\mathcal{R}$ in the jth irreducible representation. The symmetry-adapted functions are constructed to be basis functions of the point group. Furthermore, a linear combination

of the form

$$y_j^r(\mathbf{k}) = \sum_l B_l X_l^{jr}(\mathbf{k}) \tag{23}$$

is also a basis function.

We can now show that the basis function of Eq. (23) is an eigenfunction of the modified scattering kernel of Eq. (B1), and in fact is identical with the Y_n of Eq. (B1). If Eq. (23) is substituted into an expansion of the modified scattering kernel that is equivalent to Eq. (21), and the orthogonality properties of the X_l are used, then the result is a secular equation,

$$\sum_{l'} (A_{ll'}^j - \alpha\delta_{ll'}) B_{l'} = 0. \tag{24}$$

A consequence of the theorem is that the matrix of the expansion coefficients A must be Hermitian. This is shown in Appendix D for real, symmetric kernels. The eigenvalues α are thus real and the vectors of the coefficients B_l are either orthogonal or may be made orthogonal. Since the scattering eigenfunctions of Eq. (11), now labeled a_j^{rn}, are related to the eigenfunctions of Eq. (23) through the scalar function $[q(\mathbf{k})]^{1/2}$, it follows that, in the sense defined in Eq. (22), the symmetry properties of the two functions will be the same.

The meaning of the indexing of the scattering eigenvalues and eigenvectors is clarified by an examination of the structure of the coefficient matrix $A_{ll'}^j$ of Eq. (21). This matrix connects only symmetry-adapted functions that belong to the same irreducible representation of $\mathcal{G}$. In this sense, A is a diagonal block matrix of order g and each block, individually Hermitian, is indexed by the irreducible representation j. Each block will be of infinite order if the kernel is not degenerate, and the set of all eigenvalues for all blocks is the set of scattering eigenvalues. Each scattering eigenvalue α_j^n must carry two indices, one j to label the irreducible representation to which its eigenfunctions belong, and n, an ordinal number to distinguish between eigenvalues within a block. There is one additional complication, arising from irreducible representations of dimension larger than one. If an irreducible representation is of dimension n_j, then an eigenvalue α_j^n is n_j-fold degenerate, corresponding to the n_j partners of the basis set.[10]

In summary, the weak assumption that the scattering kernel $Q(\mathbf{k}, \mathbf{k}')$ is invariant under operations of the lattice point group [Eq. (20)] determines the symmetry properties of the scattering eigenfunctions. The degeneracies of the eigenvalues are easily determined, since the scattering eigenfunctions are basis functions of the group representations.

V. APPLICATIONS OF SYMMETRY PROPERTIES OF SCATTERING EIGENFUNCTIONS

The identification of the scattering eigenfunctions as basis functions for the lattice point group has two major applications in the implementation of the formalism described in this paper. First, the sheer size of the computational problem is reduced so that it is feasible to investigate the galvanomagnetic properties of metals with nontrivial scattering kernels. The computational aspects of this formalism will not be discussed in this paper, however, so we shall not pursue this line further. For our present purposes, the real usefulness of this characterization comes in the interpretation of Eqs. (14) and (17) of Sec. III. We illustrate this by considering the full cubic group O_h that is of order 48 with 10 irreducible representations. Of these representations the most important are Γ_1, the scalar representation; Γ_{15}, the representation of $\mathbf{k}$ and $\mathbf{v}_\mathbf{k}$; and Γ_{15}', the representation of the operator $\mathbf{v}_\mathbf{k} \times \nabla_\mathbf{k}$.

In the application of symmetry arguments to the integrals represented by Eq. (17), the governing principle is that the integral of any function over an energy shell will vanish unless the function contains an invariant (scalar) part.[10] Thus, since the velocity transforms as Γ_{15}, the Kronecker product of Γ_{15} with all the irreducible representations of the a_j^n requires that $g_{\mu n}$ vanish unless a_r is one of the Γ_{15}-like functions. Even more strongly,

$$g_{\mu s} = \int v_\mu(\mathbf{k}) a_j^{rn}(\mathbf{k})\, d\xi \delta_{j,\Gamma_{15}} \delta_{r\mu}, \tag{25}$$

where the s subscript on g represents the collection (j, r, n). This result means that only the Γ_{15}-like scattering eigenfunctions contribute to the conductivity through the coefficients $g_{\mu s}$. In the case of zero magnetic field the conductivity reduces to

$$\sigma_{\mu\nu} = 2e^2 \sum_n [g_{\mu n} g_{\nu n}/(1-\alpha_n)] \tag{26}$$

as a consequence of the orthogonality of the ψ_{in}'s of Eq. (13). The zero-field resistivity is then due to the Γ_{15} part of the scattering kernel.

The dependence of the conductivity on the orientation of the magnetic field arises from the eigenvectors of the $\hat{h}\cdot C$ matrix, the ψ_{in} of Eq. (15). The quantity C is the vector of the matrix elements of the operator $\mathbf{v}_\mathbf{k} \times \nabla_\mathbf{k}$. The selection rules for these matrix elements follow from the fact that $\mathbf{v}_\mathbf{k} \times \nabla_\mathbf{k}$ transforms as Γ_{15}', and hence has even parity under inversion. Thus, there can be no matrix elements of C that connect scattering eigenfunctions of opposite parity. The eigenvectors ψ_{in} that correspond to eigenvalues of the odd-parity part of C have zeros in the positions corresponding to even-parity representations. The even- and odd-parity representations are entirely disjoint in the way they determine the ψ_{in}. This disjointness settles the question that has arisen about the operator $(q-Q)^{-1}$. Since the $g_{\mu s}$ coefficients allow only Γ_{15}-like scattering eigenfunctions to contribute to the conductivity, the ψ_{in} that include the coefficients of Γ_{15} functions are entirely independent of the even-parity scattering eigenfunctions. Hence, only those scattering eigenfunctions that are odd under inversion need be included as expansion functions. Since the operator $(q-Q)^{-1}$ is singular only when it acts upon a Γ_1-like function (i.e., either a constant or a δ-function scattering function) and these

scalar functions do not appear as expansion functions, the operator is nonsingular. The detailed selection rules for the matrix elements of C are obtained from the triple Kronecker product of the irreducible representations involved.

VI. DEGENERATE SCATTERING KERNEL

Since this formalism is designed as a computational procedure for the investigation of the effects of scattering and Fermi-surface properties on the galvanomagnetic properties of metals, an analytic discussion of any physically meaningful model is quite difficult. There is, however, one model that has been discussed in connection with this problem that bears some further discussion from the standpoint of the present formalism. The Sondheimer[11] model consists of a spherical Fermi surface with a scattering kernel of the form

$$Q(\mathbf{k},\mathbf{k}')=\sum_{i,j=1}^{N} B_{ij}q_i(\mathbf{k})q_j(\mathbf{k}'), \tag{27}$$

where $\{q_i\}$ is a set of N arbitrary functions of integrable square.[11] Sondheimer introduced this scattering model on the *ad hoc* grounds that the finite dimensionality of B reduces the Boltzmann integral equation to a set of finite linear equations.

The scattering kernel has a natural expansion in terms of the symmetry-adapted functions of the crystal point group. The degenerate-kernel model is then equivalent to a truncation of Eq. (21) after an appropriate number of terms, and the functions $\{q_i\}$ are interpreted as symmetry-adapted functions. Thus, the coefficients $A_{ll'}{}^{j}$ of Eq. (21) play the role of the B_{ij} of Eq. (27).

The use of the symmetry-adapted functions, Eq. (21), as the basis for a degenerate-kernel approximation to the scattering also serves to clarify one point of difficulty in the work of Jones and Sondheimer.[11] As an example of a degenerate kernel, they chose a fourth-order polynomial, in the components of $\mathbf{k}$ and $\mathbf{k}'$, which they assumed to be positive definite. The requirement that $Q(\mathbf{k},\mathbf{k}')$ is positive and nonzero for every $\mathbf{k}$ and $\mathbf{k}'$ led to a set of inequalities for the B_{ij} coefficients. This condition is necessary but not sufficient, however, and the difficulties in this procedure can be seen by the consideration of an equivalent scattering kernel of the form

$$Q(\mathbf{k},\mathbf{k}')=A_0+\sum_{r=1}^{3}\sum_{l=1,3;\,l'=1,3} A_{ll'}{}^{\Gamma_{15}}X_l{}^{\Gamma_{15},r}(\mathbf{k})\times X_{l'}{}^{\Gamma_{15},r}{}^{*}(\mathbf{k}'), \tag{28}$$

where only the $l=1$ and $l=3$ (real) Kubic harmonics of the irreducible representation have been included. The primary differences between this kernel and the example kernel of Jones and Sondheimer are that only the terms of odd parity have been included in Eq. (28), and that the polynomial of Q in Eq. (28) is of sixth degree (including $l=l'=3$ terms). The constant term A_0 only serves to make $q(\mathbf{k})$ nonzero.

Equation (24) relates the scattering eigenvalues to the expansion coefficients $A_{ll'}{}^{j}$. Since A_0 is constant, the function $q(\mathbf{k})$ is a constant and the secular equation for Q is the same as the secular equation for $Q(\mathbf{k},\mathbf{k}')/[q(\mathbf{k})q(\mathbf{k}')]^{1/2}$. Explicitly,

$$\begin{vmatrix} A_{11}-\alpha & A_{13} \\ A_{31} & A_{33}-\alpha \end{vmatrix}=0, \tag{29}$$

where $A_{13}=A_{31}{}^{*}$ (see Appendix B). A necessary and sufficient condition that Q be positive definite is that all the eigenvalues of Q be positive and nonzero.[12] The solution of Eq. (29) then determines the allowed values of the expansion coefficients. We note that the fourth-degree polynomial of Jones and Sondheimer is equivalent to Eq. (28) with $A_{33}=0$. Any nonzero values for A_{11} and A_{13} then give rise to a negative eigenvalue, implying that such a Q is in fact not positive definite.

VII. EXAMPLE

A simple degenerate kernel of the form described above will serve to illustrate some of the points of the formalism. A spherical surface of radius unity is used as the model for the Fermi surface. The scattering kernel of Eq. (28) is used, with the coefficients chosen as $A_0=1/(4\pi)^2$, $A_{11}=0.867$, $A_{33}=0.434$, and $A_{13}=A_{31}=0.173$. This model does not represent any metal, the coefficients chosen being for illustration only.

The scalar function $q(\mathbf{k})$ is a constant, equal to $1/4\pi$, and is determined by the value given to the coefficient A_0. An effective relaxation time may be defined as $\tau_0=(q)^{-1}=4\pi$. There are three scattering eigenvalues. Two of them are obtained from the secular equation of Eq. (29) for the modified scattering kernel. The two eigenvalues are each threefold degenerate and the eigenfunctions are linear combinations of the $l=1$ and $l=3$ Γ_{15} Kubic harmonics. The remaining eigenvalue has the value unity and corresponds to a scalar (Γ_1) eigenfunction that is a constant. From the discussion earlier in this paper and in Ref. 3, we know that this eigenfunction makes no contribution to the transport properties of the model. The C matrix consists of three 6×6 matrices that connect the two sets of Γ_{15} eigenfunctions.

The galvanomagnetic properties of this simple model are shown in Figs. 1 and 2. Figure 1 shows the transverse magnetoresistance as a function of $\omega_c\tau_0$. Figure 1(a) demonstrates the high-field saturation of the transverse magnetoresistance, while Fig. 1(b) shows the low-field behavior. Figure 2 shows the Hall resistivity (lower curve) and the effective Hall constant (upper curve), obtained from a finite-difference differentiation of ρ_{xy}. The results show that the resistivity tensor is completely isotropic; i.e., these curves are independent of the direction of the applied magnetic field. In addition, the results give a vanishing longitudinal magnetoresistance for this simple model.

VIII. CONCLUSIONS

The approach described above may be thought of as a generalization of the elementary theory of galvanomagnetic effects in isotropic materials. If one examines the free-electron model with isotropic scattering within the framework of the present formalism, one finds that the simple functions $k_x \pm ik_y$ are eigenfunctions of T when the magnetic field is in the z direction. The sum over i in Eq. (9), for example, then reduces to a sum of two terms (or, in the case of σ_{zz}, to only one term) and the well-known absence of magnetoresistance results. One may attribute this to the fact that, when σ is considered as a function of the complex variable ω, the only poles of this function occur at $\omega = \pm i/\tau$. The introduction of anisotropy then modifies this result by introducing further poles on the imaginary axis at the points $\omega = \pm i/\tau_i$.

As we have already mentioned, most previous theories of galvanomagnetic properties make use of the concept of electron orbits. The special role of open orbits, which, for example, can lead to a nonsaturating magnetoresistance, has been frequently discussed.[1] Such special cases are also understood from the point of view of the present formalism. We see from inspection of Eq. (9) that the phenomenon of nonsaturation normally associated with open orbits occurs when one of the τ_i vanishes. From Eq. (15) we note that this will be associated with the singularity of the matrix $\hat{h}\cdot C$,

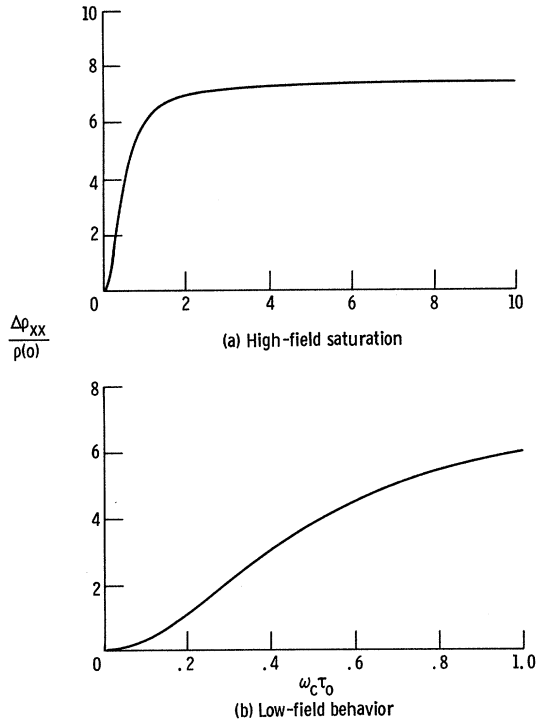

FIG. 1. Transverse magnetoresistance.

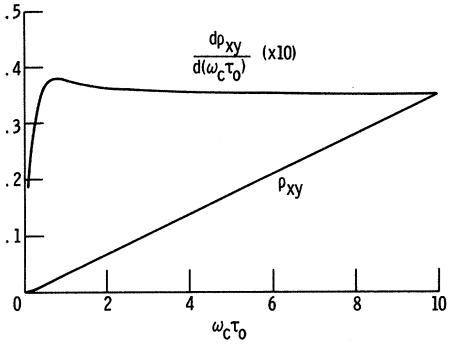

FIG. 2. Hall resistivity and effective Hall constant ($\times 10$).

and from Eq. (8) that such terms contribute no field dependence to $\sigma_{\mu\nu}$.

The convenience of the scattering-eigenfunction approach is now apparent. The major part of the labor necessary to solve the Boltzmann equation is performed in the evaluation of the scattering eigenfunctions $a_n(\mathbf{k})$ and their associated eigenvalues α_n, *in the absence of the magnetic field.* When now a given direction $\hat{h}$ of the magnetic field is considered, it becomes a simple matter to form the matrix $\hat{h}\cdot C$ and to find its eigenfunctions and eigenvalues, and hence the conductivity tensor. Detailed computations for some realistic models are now in progress and will be reported in a later publication.

APPENDIX A: PROPERTIES OF MAGNETIC SCATTERING OPERATOR

The properties of the magnetic scattering operator T may be obtained from consideration of a more general operator

$$T = Q^{-1}P, \tag{A1}$$

where P and Q (and hence Q^{-1}) are Hermitian. The operator T will not be Hermitian unless P and Q^{-1} commute. If Q is assumed to be a positive definite, bounded, linear operator, then the operator $Q^{1/2}$ exists.[13]

Instead of T, it is more convenient to work with a new operator

$$T' = Q^{-1/2}PQ^{-1/2}. \tag{A2}$$

Since T' is constructed to be Hermitian, it has eigenvalues and eigenfunctions defined by

$$T'x_n = Q^{-1/2}PQ^{-1/2}x_n = \tau_n x_n, \tag{A3}$$

where τ_n is real and the $\{x_n\}$ form a complete, orthonormal set of eigenfunctions. Operating on the left-hand side of Eq. (A3) with $Q^{-1/2}$ gives

$$Q^{-1}P(Q^{-1/2}x_n) = \tau_n(Q^{-1/2}x_n),$$

or

$$T(Q^{-1/2}x_n) = \tau_n(Q^{-1/2}x_n). \tag{A4}$$

A comparison of Eqs. (A4) and (A1) shows that the eigenvalues of T are the same as the eigenvalues of T'. Furthermore, the eigenfunctions of T' (i.e., $Q^{-1/2}x_n$) are complete since the x_n are complete and Q is a positive definite, bounded linear operator.

This discussion is applied to the magnetic scattering operator T by the association

$$Q\rightarrow(q-Q),$$
$$P\rightarrow(im/\hbar)(\mathbf{v}_\mathbf{k}\cdot\hat{h}\times\nabla_\mathbf{k}).$$

Thus, since the τ_n are real, the quantity $i\omega_c\tau_n$ is an imaginary number and $(1-i\omega_c T)^{-1}$ is nonsingular.

This discussion is not a rigorous justification of the expansion in terms of the magnetic scattering eigenfunctions used in the text. The difficulty lies in the fact that P, a derivative operator, is not bounded. Hence, there is no guarantee that the eigenfunctions of T lie in the space spanned by the scattering eigenfunctions $a_n(\mathbf{k})$, and the question then is the existence of the expansion of Eq. (10) for the b_i in terms of the a_n. The ultimate justification for this expansion is that the expansion coefficients γ_{in} are obtained, independently, through Eq. (15).

APPENDIX B: PROPERTIES OF SCATTERING OPERATOR

Equation (11) defines the scattering eigenfunctions $a_n(\mathbf{k})$ and the scattering eigenvalues α_n of the scattering operator $q^{-1}Q$. It has been observed[3] that this scattering operator is not Hermitian, so that the scattering eigenfunctions are not orthogonal. In a manner similar to that used in Appendix A, the properties of the scattering operator may be obtained by considering an equivalent scattering operator defined by the eigenvalue equation

$$\int\frac{Q(\mathbf{k},\mathbf{k}')}{[q(\mathbf{k})q(\mathbf{k}')]^{1/2}}Y_n(\mathbf{k}')\,d\mathbf{k}'=\alpha_n Y_n(\mathbf{k}),\quad\text{(B1)}$$

where

$$d\mathbf{k}=[2/(2\pi)^3](d\mathcal{E}_\mathbf{k}dS/\hbar\mid\mathbf{v}_\mathbf{k}\mid)=d\xi d\mathcal{E}_\mathbf{k}.$$

The kernel of Eq. (B1) is real, positive definite, and symmetric, so the set of eigenfunctions $\{Y_n\}$ are orthogonal. Since the assumption of elastic scattering requires that $Q(\mathbf{k},\mathbf{k}')$ be proportional to an energy-conserving δ function, the scattering eigenfunction may be separated into the product of an energy-dependent part and a part that only depends upon the surface variable ξ. The resulting scattering-eigenvalue equation is

$$\int\frac{\mathcal{Q}(\mathbf{k},\mathbf{k}')}{[q(\mathbf{k})q(\mathbf{k}')]^{1/2}}Y_n(\mathbf{k}')\,d\xi'=\alpha_n Y_n(\mathbf{k}).\quad\text{(B2)}$$

The orthogonality condition for the eigenfunctions of Eq. (B2) follows from the symmetry of the kernel

$$\int Y_n(\mathbf{k})Y_r(\mathbf{k})\,d\xi=\delta_{rn}.\quad\text{(B3)}$$

The scattering eigenfunctions $a_n(\mathbf{k})$ may be recovered by the definition

$$a_n(\mathbf{k})=Y_n(\mathbf{k})/[q(\mathbf{k})]^{1/2}.\quad\text{(B4)}$$

Hence, from Eq. (B3) we get the desired orthogonality condition for the $\{a_n\}$

$$\int a_n(\mathbf{k})q(\mathbf{k})a_r(\mathbf{k})\,d\xi=\delta_{rn}.\quad\text{(B5)}$$

APPENDIX C: HERMITICITY OF C_{rn}

The vector matrix C_{rn} was defined in (Eq. 14) as

$$C_{rn}=-\{im/\hbar[(1-\alpha_r)(1-\alpha_n)]^{1/2}\}\times\int a_r(\mathbf{k})(\mathbf{v}_\mathbf{k}\times\nabla_\mathbf{k})a_n(\mathbf{k})\,d\xi$$

or, equivalently,

$$C_{rn}=-\{im/\hbar[(1-\alpha_r)(1-\alpha_n)]^{1/2}\}\times\int a_r(\mathbf{k})(\mathbf{v}_\mathbf{k}\times\nabla_\mathbf{k})a_n(\mathbf{k})\delta(\mathcal{E}_\mathbf{k}-\mathcal{E}_F)\,d\mathbf{k}.$$

To prove that C is Hermitian we consider the vector quantity

$$\nabla_\mathbf{k}\times(\eta\mathbf{v}_\mathbf{k})=\eta\nabla_\mathbf{k}\times\mathbf{v}_\mathbf{k}-\mathbf{v}_\mathbf{k}\times\nabla_\mathbf{k}\eta,$$

where η is a scalar function of $\mathbf{k}$. Since $\mathbf{v}_\mathbf{k}$ is $\nabla_\mathbf{k}\mathcal{E}_\mathbf{k}/\hbar$, $\nabla_\mathbf{k}\times\mathbf{v}_\mathbf{k}=0$. Hence

$$\nabla_\mathbf{k}\times[a_r a_n\delta(\mathcal{E}_\mathbf{k}-\mathcal{E}_F)\mathbf{v}_\mathbf{k}]=-[\mathbf{v}_\mathbf{k}\times\nabla_\mathbf{k}a_r]a_n\delta(\mathcal{E}_\mathbf{k}-\mathcal{E}_F)-[\mathbf{v}_\mathbf{k}\times\nabla_\mathbf{k}a_n]a_r\delta(\mathcal{E}_\mathbf{k}-\mathcal{E}_F),$$

the remaining term vanishing since $\nabla_\mathbf{k}\delta(\mathcal{E}_\mathbf{k}-\mathcal{E}_F)$ is in the direction of $\mathbf{v}_\mathbf{k}$.

Now we consider the integral of the factor $\nabla_\mathbf{k}\times(\eta\mathbf{v}_\mathbf{k})$,

$$\int\nabla_\mathbf{k}\times(\eta\mathbf{v}_\mathbf{k})\,d\mathbf{k}=\int\eta\mathbf{v}_\mathbf{k}\times\hat{n}\,dS,$$

where $\hat{n}$ is the unit normal to the Fermi surface. Since $\mathbf{v}_\mathbf{k}$ is everywhere in the direction of $\hat{n}$, the vector product vanishes. Thus,

$$\int a_r(\mathbf{k})[\mathbf{v}_\mathbf{k}\times\nabla_\mathbf{k}]a_n(\mathbf{k})\delta(\mathcal{E}_\mathbf{k}-\mathcal{E}_F)\,d\mathbf{k}=-\int a_n(\mathbf{k})[\mathbf{v}_\mathbf{k}\times\nabla_\mathbf{k}]a_r(\mathbf{k})\delta(\mathcal{E}_\mathbf{k}-\mathcal{E}_F)\,d\mathbf{k},$$

or

$$C_{rn}=-C_{nr}=C_{nr}{}^*.$$

Therefore C is Hermitian.

APPENDIX D: GROUP-THEORETIC RESULTS FOR SEC. IV

The theorem quoted in Sec. IV is easily obtained from the representation theory of finite groups and the properties of the symmetry-adapted functions. For the case of spherically symmetric kernels and spherical harmonics this theorem is well known. Its natural extension to point groups and the symmetry-adapted functions does not appear to have been noticed.

The theorem, to be proven here, is a statement about the form of the kernel $Q(\mathbf{k},\mathbf{k}')$ as an expansion in the symmetry-adapted functions. Certainly, since $Q(\mathbf{k},\mathbf{k}')$ may be considered successively as a function of $\mathbf{k}$ and then as a function of $\mathbf{k}'$, there exists the general expan-

sion

$$Q(\mathbf{k},\mathbf{k}')=\sum_{ljr}\sum_{l'j'r'}A_{ll'}{}^{jrj'r'}X_l{}^{jr}(\mathbf{k})X_{l'}{}^{j'r'}{}^*(\mathbf{k}'). \quad \text{(D1)}$$

The proof of the theorem must demonstrate that the group symmetry of Q requires that the expansion coefficients only depend upon l, l', and j. Thus,

Theorem. Given a function $Q(\mathbf{k},\mathbf{k}')$ that is invariant under all operations $\mathfrak{R}$ of a group $\mathfrak{G}$ [i.e., $Q(\mathbf{k},\mathbf{k}')=Q(R\mathbf{k},R\mathbf{k}')$ for all $\mathfrak{R}$ of $\mathfrak{G}$], then there exists the expansion

$$Q(\mathbf{k},\mathbf{k}')=\sum_{llj}A_{ll'}{}^{j}\sum_{r}X_l{}^{jr}(\mathbf{k})X_{l'}{}^{jr}{}^*(\mathbf{k}'). \quad \text{(D2)}$$

Proof. The proof follows from an explicit evaluation of $Q(R\mathbf{k},R\mathbf{k}')$. Since the symmetry-adapted functions are basis functions for the point group, $X_l{}^{jr}(R\mathbf{k})$ can be written in terms of $X_l{}^{js}(\mathbf{k})$. The orthogonality property of $X_l{}^{jr}$ along with the symmetry requirement on the $Q(\mathbf{k},\mathbf{k}')$ gives

$$A_{ll'}{}^{jrj'r'}=\sum_{pp'}A_{ll'}{}^{jpj'p'}D_{rp}{}^{(j)}{}^*(R)D_{r'p'}{}^{(j')}(R). \quad \text{(D3)}$$

The matrices of the irreducible representations of $\mathfrak{G}$ have an orthogonality condition that[10]

$$\sum_{R}D_{rs}{}^{(j)}(R)D_{pq}{}^{(j')}{}^*(R)=(g/n_j)\delta_{rp}\delta_{sq}\delta_{jj'}. \quad \text{(D4)}$$

Thus a summation of Eq. (D3) over all group elements yields

$$A_{ll'}{}^{jrj'r'}=(1/n_j)\sum_{pp'}A_{ll'}{}^{jpj'p'}\delta_{jj'}\delta_{rr'}\delta_{pp'}$$

or, after all extraneous indices are removed,

$$A_{ll'}{}^{jr}=(1/n_j)\sum_{p}A_{ll'}{}^{jp}.$$

Since this relation must hold for all n_j values of r, it is clear that $A_{ll'}{}^{jr}$ in fact cannot depend upon the column index r and the theorem is proved.

It is appropriate at this point to use Eq. (25) to demonstrate two points that have been made in the text. The first is the Hermiticity of the coefficient matrix $A_{ll'}{}^{j}$. Since $Q(\mathbf{k},\mathbf{k}')$ is assumed to be a real, symmetric kernel, evaluation of Eq. (21) for $Q(\mathbf{k},\mathbf{k}')$ and $Q^*(\mathbf{k}',\mathbf{k})$ gives immediately that $A_{ll'}{}^{j}=A_{l'l}{}^{j}{}^*$.

The other point to be made concerns the function $q(\mathbf{k})$, the integral of Eq. (21) over the surface dS'. The simplest way to illustrate the properties of $q(\mathbf{k})$ is to assume that the Fermi surface is spherical, i.e., the magnitude of the Fermi velocity is a constant everywhere on the surface. Thus, if Eq. (21) is integrated over dS', the orthogonality of the symmetry-adapted functions leaves only the $l'=0$ term; that is,

$$q(\mathbf{k})=\sum_{l}A_{l0}{}^{\Gamma_1}X_l{}^{\Gamma_1}(\mathbf{k}),$$

a scalar function (Γ_1) of $\mathbf{k}$.

For a nonspherical surface the magnitude of the Fermi velocity, though not constant, is a scalar. Thus, the integral over dS' involves an integral of a product of $X_{l'}{}^{jr}{}^*$ with a linear combination of scalar symmetry-adapted functions (i.e., $j=\Gamma_1$, but here l' is not restricted to 0), and the result is clearly still a scalar.

* Supported in part by the U.S. Atomic Energy Commission.

[1] A. B. Pippard, Rept. Progr. Phys. **23**, 176 (1960).
[2] P. L. Taylor, *A Quantum Approach to the Solid State* (Prentice-Hall, Englewood Cliffs, N.J., 1970).
[3] P. L. Taylor, Proc. Roy. Soc. (London) **A275**, 200 (1963).
[4] R. G. Chambers, Proc. Phys. Soc. (London) **A65**, 458 (1952); A. B. Pippard, *ibid.* **A282**, 464 (1964).
[5] J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, England, 1960).
[6] Reference 3, p. 207.
[7] M. A. Melvin, Rev. Mod. Phys. **28**, 18 (1956).
[8] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).
[9] E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic, New York, 1959), Chap. 11.
[10] M. Hamermesh, *Group Theory and Its Application to Physical Problems* (Addison-Wesley, Reading, Mass., 1962), Chap. 6.
[11] M. C. Jones and E. H. Sondheimer, Phys. Rev. **155**, 567 (1967).
[12] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), Vol. 1, Chap. 3.
[13] E. Riesz and B. Sz.-Nagy, *Functional Analysis* (Ungar, New York, 1955), Chap. 7.