Hall Mobility of the Small Polaron. II

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A perturbation treatment of Kubo's basic formula for the electrical-conductivity tensor is used to derive an expression for the Hall mobility of the small polaron. The result disagrees with those of other treatments based on Kubo's formula, but coincides completely with that obtained previously by the present authors via a jump-probability approach.

I. INTRODUCTION

In a previous paper, with the above title,[1] the present authors have developed a treatment of the Hall mobility of the small polaron, based on a physically intuitive jump-probability approach. In this approach, the Hall current is regarded as arising from the modification, by an external magnetic field, of the elementary two-site jump-rate (i.e., the probability per unit time for the occurrence of a charge-carrier jump between two atomic sites). As shown in the cited work, such a modification—in particular, one which is linear in the magnetic field—arises from the interference between the first-order amplitude for a direct jump between the sites and the second-order amplitude, involving intermediate occupancy of a third site.[2] From elementary kinetic considerations, it is then deduced that the transverse mobility μ_{xy} (related to the transverse conductivity σ_{xy} by the relation $\sigma_{xy}=-ne\mu_{xy}$, where n is the density of charge-carriers—assumed to be electrons for the sake of definiteness) contains a component which is linear in the magnetic field, and which is hence a direct manifestation of a nonvanishing Hall effect.

Subsequently, two additional treatments of the problem have been published, the first by Firsov[3] and the second by Schnakenberg.[4] The approach of both these treatments consists of a perturbation expansion (in powers of J) of the basic Kubo expression for the transverse conductivity, σ_{xy}—more correctly, its antisymmetric part, $\sigma_{xy}{}^{(a)}\equiv\frac{1}{2}(\sigma_{xy}-\sigma_{yx})$, this being the component relevant for the Hall effect. Results contradictory to each other and to those of FH were obtained, the differences being especially striking with respect to the temperature variation. Specifically, Firsov finds μ_{xy} to be inversely proportional to T. [Apart from the factor $\beta\equiv 1/\kappa T$, the temperature does not appear in his Eq. (21).] In particular, there is nothing suggestive of an activation process. Since the temperature dependence of the diagonal component of the mobility tensor μ_{xx} is predominantly of the activation form[5] $e^{-E_a/\kappa T}$, it follows that the Hall mobility μ_H as defined by the relationship $\mu_H H/c=\mu_{xy}{}^{(a)}/\mu_{xx}=\sigma_{xy}{}^{(a)}/\sigma_{xx}$ varies with temperature essentially as $e^{E_a/\kappa T}$, i.e., a *negative activation* dependence.

In Schnakenberg's paper [cf. his Eqs. (3.21) and (2.8)], the temperature dependence of $\mu_{xy}{}^{(a)}$ is predominantly of the form $e^{-E_a/\kappa T}$, i.e., the same as that of μ_{xx}. It then follows that μ_H varies only weakly with temperature (because of the presence of algebraic factors, ignored in this discussion).

In FH, it is found that the temperature dependence of $\mu_{xy}{}^{(a)}$ is also of the activation type ($\sim e^{-E_a'/\kappa T}$), where, however, in contrast to Schnakenberg's result, the activation energy E_a' is larger than E_a; in particular, it is found that

$$E_a'=(4/3)E_a.$$

It then follows that μ_H possesses an activation-type temperature ($\sim e^{-(E_a'-E_a)/\kappa T}=e^{-E_a/3\kappa T}$), albeit, with a considerably smaller activation energy than that associated with the drift mobility $\mu_D\equiv\mu_{xx}$.

From the standpoint of the jump-probability approach, a result such as Schnakenberg's would be attributed—just as in FH—to processes involving interference between the amplitude for a direct jump between two sites and that for the two-stage process, involving intermediate occupancy of a third site, with, however, the important difference that the energy of the intermediate state be noncoincident with the initial energy. In the language of FH, such transitions would be of the "two-site coincidence" type—i.e., transitions in which the energies of initial and final states coincide (as, of

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[1] L. Friedman and T. Holstein, Ann. Phys. (N. Y.) **21**, 494 (1963), to be denoted hereafter as FH. For a description of the basic concepts of small polaron theory, see, e.g., T. Holstein, *ibid.* 8, 325, 343 (1959).

[2] Here, it is tacitly assumed that each site has two nearest neighbors, which are nearest neighbors of each other (e.g., as in a two-dimensional hexagonal lattice, or in a fcc lattice). In other cases, the interference is necessarily a higher-order process. Only the former case will be considered in the present paper.

[3] Yu. A. Firsov, Fiz. Tverd. Tela **5**, 2149 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1566 (1964)].

[4] J. Schnakenberg, Z. Physik **185**, 123 (1965).

[5] Strictly speaking, the activation-type dependence is realized only in the classical limit $T\gg\Theta$ (Θ=Debye temperature). It may be remarked that [T. Holstein, Ann. Phys. (N. Y.) 8, 343 (1959), Fig. 1] quantal departures from the classical limit are small even at $T\cong\Theta$.

course, they must, in order for the over-all transition to be real, rather than virtual). In this respect, they would be similar to the zeroth-order direct transitions between two sites; it is hence not surprising that their activation-type temperature dependence is identical.[6]

However, it is a cardinal feature of the treatment of FH that the contributions of the three-site transitions in which intermediate energy is not conserved cancel in detail; the final expression for that part of the site-jump probability which is linear in the magnetic field—this component being the one relevant for the Hall effect—involves only three-site transitions in which intermediate (as well as final) energy coincides with the initial energy.[7]

In the case of Firsov's result for $\mu_{xy}{}^{(a)}$, the absence of any activation factor in its temperature dependence does not appear to be capable of interpretation in terms of a jump-probability picture. In particular, such an interpretation would have to explain how the application of a magnetic field (however small) gives rise to a transverse motion of charge carriers which is *unimpeded* by energy barriers, whereas thermal activation for charge-carrier motion parallel to the electric field is still required.

From the above discussion, it is seen that, were either Schnakenberg's or Firsov's results to be valid, one would have to conclude that the Hall effect is simply uninterpretable in terms of elementary jump-probability concepts. Indeed, Firsov essentially asserts this conclusion in his final comment (bottom rhs of p. 1579 of Ref. 3).

In view of the above outlined situation, the present authors have felt it necessary to attempt a rederivation of their former results via a treatment based on the same starting point as those of Firsov and Schnakenberg—namely, Kubo's conductivity formula. This rederivation has been achieved; it constitutes the subject matter of the present paper.

Section I and Appendix A are devoted to a recapitulation of the basic elements of small polaron theory. In Sec. II, this theory is used in conjunction with Kubo's conductivity formula to derive an expression [Eq. (3.35)] for $\sigma_{xy}{}^{(a)}$; this result is then shown to be straightforwardly derivable from FH's basic "three-site probability" expression, given by the last equation on p. 515 of their article. A cardinal feature of Eq. (2.34) is the presence of two energy-conserving delta functions on its rhs—exhibiting the fact that only those transitions in which intermediate (as well as final) energy is conserved, contribute to the Hall effect in hopping-type charge transport. As pointed out above, it is this requirement which is ultimately responsible for the appearance of the activation factor $e^{-E_a'/\kappa T}$ in the final expressions for $\sigma_{xy}{}^{(a)}$ and $\mu_{xy}{}^{(a)}$.

II. BASIC PRELIMINARIES

The treatment given here is based on a generalized "hopping-model" Hamiltonian of the form

$$\langle jn_j|H|in_i\rangle=\epsilon_i(n_i)\delta_{ij}\delta_{n_in_j}+\langle n_j|V_{ji}{}^{(H)}|n_i\rangle. \quad (2.1)$$

It is presupposed that the state of the system, consisting of a single electron (hole) plus lattice vibrations, can be described as a superposition of "basic" states $|i,n_i\rangle$ in which the electron (hole) is located at site i and the lattice is in a given vibrational state, specified by a set of vibrational quantum numbers, $\cdots N_\lambda{}^{(i)}\cdots$, denoted collectively by the symbol n_i. The detailed expressions for these basic states, as well as those for the terms on the rhs of (1) are developed in Appendix A[8] [cf. Eqs. (A40)–(A45)]. Here, let us note briefly that the vibrational states associated with electron (hole) occupancy of a particular (ith) site are [cf. Eq. (A40) harmonic-oscillator functions, not of the normal coordinates Q_λ of the host lattice, but rather of "displaced" coordinates, $Q_\lambda-Q_\lambda{}^{(i)}$, corresponding to a shift in the equilibrium position of the lattice ions produced by their interaction with the electron (hole) localized at the ith site. It then follows that, in contrast to the usual tight-binding treatments (in which the lattice-vibrational state is described in terms of a fixed basis, independent of the state of the excess charge-carrier), the charge-transfer term $\langle n_j|V_{ji}{}^{(H)}|n_i\rangle$ (giving rise to intersite transitions of the charge carrier) is *not diagonal in the lattice quantum numbers* n_i. As shown by its specific form [cf. Eq. (A44)], it contains nonvanishing matrix elements for transitions of the type ($i\rightarrow j$; $N_\lambda{}^{(j)}=N_\lambda{}^{(i)}$, $N_\lambda{}^{(i)}\pm1$), i.e., transitions in which the phonon population of each mode may change by ±1 or zero.

Let us furthermore note that [cf. Eq. (A44)] the charge-transfer term may be written in the form

$$\langle n_j|V_{ji}{}^{(H)}|n_i\rangle=e^{i\alpha_{ji}}\langle n_j|V_{ji}|n_i\rangle, \quad (2.2)$$

where $\langle n_j|V_{ji}|n_i\rangle$ is independent of the magnetic field; the field dependence is contained solely in the phase factors α_{ji} as expressed by the fundamental relation [cf. (A18) and (A19)]

$$\alpha_{ji}+\alpha_{kj}+\alpha_{ik}=-(e/\hbar c)\mathbf{H}\cdot\mathbf{A}_{kji}, \quad (2.3)$$

[6] As shown in FH's Appendix B—in connection with the classical occurrence-probability approach of their Sec. II (in which the lattice motion is treated classically)—the activation energy E_a is the minimum vibrational energy required to effect a lattice displacement such that the *electronic energies* of two sites (including electron-lattice interaction)—are brought into coincidence. In contrast, the energy E_a' is the vibrational energy required to effect a coincidence in the electronic energies of three sites ("three-site coincidence").

[7] This feature is shown explicitly in the last equation on p. 515 of FH. Namely, upon augmenting the explicitly written term on the rhs of this equation with its complex conjugate (as indicated), the result is seen to be proportional to the product of two energy-conserving delta functions—one whose argument is equal to the difference between initial and final energies, the other equal to the difference between initial and intermediate energies. Note, especially, that the term proportional to the principal value of the reciprocal of the latter energy difference is purely imaginary; it is hence cancelled by its complex conjugate.

[8] Apart from certain generalizations, this Appendix is essentially a recapitulation of FH's Sec. II and pp. 511–513. It is given here for the purpose of providing a self-contained presentation, which, in addition, is not based on the specific two-dimensional molecular-crystal model of FH.

namely, the sum of the phase factors around a closed circuit of intersite transitions is equal to $(-e/\hbar c)$ times the flux through the area bounded by the intersite vectors defining the circuit.[9]

For the purposes of subsequent analysis, it is desirable to make explicit mention of an additional property of the charge-transfer term, namely, its reality in the limit of zero magnetic field, i.e.,

$$\langle n_j|V_{ji}|n_i\rangle=\langle n_j|V_{ji}|n_i\rangle^*. \tag{2.4}$$

The validity of (2.4) may be checked directly by inspection of Eq. (A44) of Appendix A; from the text material preceding that equation, it is clear that (4) rests upon the choice of a standing-wave description of lattice-vibration modes [cf. Eqs. (A33) and (A34)].[10]

An additional property of the Hamiltonian, which will be utilized in the treatment, is the fact that the spectrum of the "local-site" energy $\epsilon_i(n_i)$ is densely discrete, i.e., in effect continuous. Inspection of Eq. (A42) shows that, apart from a constant (which in some cases may depend on site index), the spectrum is that of the lattice vibrations of the host crystal; this spectrum is continuous provided that account is taken of the frequency dispersion of the normal-mode frequencies[11] ω_λ.

For the purpose of developing a formal theory of conductivity, one final specification is required, namely, an expression for the charge-carrier velocity operator. Here, two alternate procedures suggest themselves. One is simply to project the usual single-particle velocity operator, $(\hbar/im)\mathrm{grad}_\mathbf{r}+e\mathbf{A}/mc$, onto the subspace spanned by the basis $|i,n_i\rangle$. The other is to project the position operator $\mathbf{r}$ onto this *subspace*, and to *define* the velocity operator as $i/\hbar$ times the commutator of the projected position operator with the Hamiltonian (2.1); thus

$$\langle j,n_j|\mathbf{v}|i,n_i\rangle\equiv\frac{i}{\hbar}\sum_{k,n_k}\{\langle j,n_j|H|k,n_k\rangle\langle k,n_k|\mathbf{r}|i,n_i\rangle - \langle j,n_j|\mathbf{r}|k,n_k\rangle\langle k,n_k|H|i,n_i\rangle\}. \tag{2.5}$$

This second procedure, together with the additional simplification of neglecting matrix elements of $\mathbf{r}$ between different sites, i.e., introducing the "site" approximation[12]

$$\langle jn_j|\mathbf{r}|i,n_i\rangle\rightarrow\delta_{ij}\langle in_j|\mathbf{r}|in_i\rangle=\delta_{ij}\delta_{n_in_j}\mathbf{R}_i \tag{2.6}$$

yields, with use of (2.1),

$$\langle jn_j|\mathbf{v}|in_i\rangle=\frac{i}{\hbar}\langle n_j|V_{ji}^{(H)}|n_i\rangle\mathbf{R}_{ji}, \tag{2.7}$$

where

$$\mathbf{R}_{ji}\equiv\mathbf{R}_j-\mathbf{R}_i. \tag{2.8}$$

Some discussion of the above procedure is now in order. First of all, with regard to the definition of the velocity operator via Eq. (2.5), rather than as the aggregate of the matrix elements $(1/m)\langle jn_j|(\hbar/i)\mathrm{grad}_\mathbf{r}+(e\mathbf{A}/c)|in_i\rangle$, it should be noted that the two definitions would coincide, were the basis set $|i,n_i\rangle$ complete. As is known, however, the $\Phi_i(\mathbf{r})$ (which express the dependence of the basic states on the charge-carrier coordinate) lack this property; i.e., an arbitrary function of $\mathbf{r}$ is *not* representable as a superposition of the $\Phi_i(\mathbf{r})$. It then follows that, within the framework of the present treatment, in which an arbitrary state of the system it represented as a superposition of the $\Phi_i(\mathbf{r})$, the Hamiltonian defined by (2.1) operates only within the subspace spanned by the $\Phi_i(\mathbf{r})$. Such a projected Hamiltonian is different from the original Hamiltonian, given by Appendix Eqs. (A1) and (A2); it is hence not surprising that the associated velocity operator differs from the standard one.

The choice of (2.5) as the definition of the velocity operator guarantees that, within the framework of a treatment based on (2.1), the expectation value of the charge-carrier velocity is equal to the time derivative of the expectation value of the charge-carrier position, thereby ensuring particle conservation. In the opinion of the present authors, this feature is a mandatory requirement for an internally consistent theory.

There remains the question of the neglect of the intersite matrix elements of $\mathbf{r}$, as embodied in (1.6). The justification for this step may be stated as follows.

(1) Of immediate relevance to the present paper, the use of (2.6) leads to an expression for the matrix elements of the velocity operator [cf. Eq. (2.7)] which is in essential agreement with those used in the European papers.[13] Since a principal objective of the present work is a critique of those papers, the desirability of basing the treatment on the same model is self-evident.

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[9] Strictly speaking, Eq. (2.3) refers to a three-site circuit; however, the generalization to an n-site circuit is obvious. It may also be remarked here that, under certain circumstances [cf. T. Holstein, Phys. Rev. **124**, 1329 (1961); **124**, 1332 (1961)], the quantity $\mathbf{A}_{kji}$ may not correspond precisely to the above-defined geometrical area; it should, however, in all cases be of comparable order.

[10] It is of course possible to employ running-wave modes in the formalism; in that case one finds that, in place of (2.4), there exist adjoint relationships between the amplitudes for emission (absorption) of phonons of any given running mode with corresponding amplitudes for the "time-reversed" mode [cf. Eq. (A31) and preceding text].

[11] As shown in the earlier papers [cf., e.g,. T. Holstein, Ann. Phys. (N. Y.) 343 (1959)] on small-polaron theory, it is necessary to take account of this dispersion—at least in principle—in order to obtain meaningful results for transition probabilities.

[12] The *equality* in (2.6) follows from the explicit form of the basis set, given by Eq. (A40), together with the additional relationship $\mathbf{R}_i=\int|\Phi(\mathbf{r}-\mathbf{R}_i)|^2d^3r$. The latter equation is valid under the various symmetry conditions postulated in the treatment of Appendix A.

[13] Refer to Eq. (1.7) of Ref. 4, and the paragraph preceding Eq. (23) of I. G. Lang and Yu. A. Firsov, Zh. Eksperim i Teor. Fiz. **43**, 1843 (1962) [English transl.: Soviet Phys.—JETP **16**, 1301 (1963)]. In Firsov's Hall-effect paper (Ref. 3), which constitutes an extension of Lang and Firsov, additional contributions to the velocity operator, linear in the magnetic field, appear [cf. his Eqs. (12a) and (12b)]. However [cf. his Eqs. (17)–(19)], these terms apparently cancel out in the final result for the Hall-conductivity $\frac{1}{2}(\sigma_{xy}-\sigma_{yx})$ (as evidenced by its proportionality to the flux through the area of the basic three-site triangle; the extra terms would give rise to a different geometrical dependence). It should be stated that the velocity matrix elements quoted from these papers are taken in the "undisplaced lattice-coordinate" representation, in which the lattice eigenfunctions $\chi_{N\lambda}(Q_\lambda)$ are those of the host lattice [rather than the displaced eigenfunctions of Eq. (A40) of Appendix A of this paper]. This point should be kept in mind in comparing the quoted expressions with Eq. (2.7) of the present paper.

(2) Of more general interest is the question as to whether the inclusion of the intersite matrix elements of position can lead to *new* effects for the Hall conductivity. A study of this question is presently being carried out, and will (hopefully) be reported in a future paper by one of the present authors (TH). The principal features emerging from this study may be summarized as follows:

(a) Subject to the symmetry assumptions introduced in Appendix A of the present paper—in particular, spherical symmetry, or cylindrical symmetry about the magnetic-field direction—it is readily shown that the intersite matrix elements of $\mathbf{r}$ are (1) linear in the magnetic field, and (2) depend only on the "relative" site-coordinate $\mathbf{R}_{ji}$.

(b) The "intersite-coordinate" operator $\mathbf{r}^{(2)}$ defined by the matrix equation

$$\langle j,n_j|\mathbf{r}^{(2)}|i,n_i\rangle\equiv(1-\delta_{ji})\langle j,n_j|\mathbf{r}|i,n_i\rangle$$

may be shown to be bounded, in the sense that the expectation value of $\mathbf{r}^{(2)}$ in an arbitrary state is bounded.[14]

(c) One now focuses attention on the contributions to the dc Hall conductivity, which arise from the existence of the additional velocity-term

$$\mathbf{v}^{(2)}\equiv(i/\hbar)(H\mathbf{r}^{(2)}-\mathbf{r}^{(2)}H)$$

[with H given by (2.1)] associated with the intersite-coordinate operator $\mathbf{r}^{(2)}$. On physical grounds, such contributions would be expected to be nonexistent, by virtue of the fact that, since $\mathbf{v}^{(2)}$ is the time-derivative of a bounded operator, the long-time average of its expectation value in an arbitrary state is zero. This intuitive consideration is confirmed by detailed calculation. In particular, it has been shown that no contributions of $\mathbf{v}^{(2)}$ to the Hall conductivity occur up to third order[15] in the overlap parameter S_{ji} [defined by Eq. (A10) of Appendix A]. Moreover, preliminary calculations indicate that the absence of such contributions can be proved to all orders in the overlap parameter.

In view of the above remarks, the neglect of the intersite-coordinate operator $\mathbf{r}^{(2)}$ as embodied in Eq. (2.6) will be incorporated into the treatment. One is then left with Eqs. (2.1), (2.2), (2.3), (2.4), and (2.7); these equations constitute the basis of the calculation for the Hall conductivity, to be given in the following section.

III. HALL CONDUCTIVITY

The basic starting point of the calculation of the Hall conductivity,

$$\sigma_{xy}{}^{(a)}\equiv\tfrac{1}{2}(\sigma_{xy}-\sigma_{yx}), \tag{3.1}$$

is a Kubo-type relationship, the specific form of which reads

$$\sigma_{xy}(\omega)=\frac{e^2\hbar}{i\Omega V}[\mathfrak{F}_{xy}(\Omega)-\mathfrak{F}_{xy}(0)]. \tag{3.2}$$

In this expression e and $\hbar$ have their conventional meanings, V is the volume of the sample, and $\Omega\equiv\hbar(\omega+is)$ (with ω the frequency of the applied electric field and s an infinitesimally small, positive quantity). Finally, $\mathfrak{F}_{xy}(\Omega)$ is the analytic continuation (regular throughout the complex Ω plane, with the exception of a possible discontinuity on the real axis) of the "thermodynamic" velocity-correlation function

$$\mathfrak{F}_{xy}(\hbar\omega_r)\equiv\int_0^\beta e^{\hbar\omega_r u}\frac{1}{Z}\,\mathrm{Tr}\{e^{-H(\beta-u)}v_x e^{-uH}v_y\}du, \tag{3.3}$$

where $\beta\equiv1/\kappa T$ (κ=Boltzmann's constant).

$$\omega_r=2\pi ir/\beta\hbar;\ r\ \text{integral}, \tag{3.4}$$

$$Z=\mathrm{Tr}\{e^{-\beta H}\}. \tag{3.5}$$

H is the Hamiltonian operator [given explicitly by (2.1)] and v_x, v_y are the Cartesian components of the charge-carrier velocity operator [given by (2.7)].

The equivalence of (3.2) to the standard Kubo formula is readily established; the details of the proof are presented in Appendix B.

Following the program of the European papers,[3,4] let us compute $\sigma_{xy}{}^{(a)}$ to third order in the transfer term, $\langle n_j|V_{ji}{}^{(H)}|n_i\rangle$, of (2.1). Now from (2.7), it is apparent that the velocity operator is proportional to this term; hence, two powers of the transfer-parameter J [cf. (A44)] occur already in the zeroth-order contributions of (3.3)—i.e., those contributions resulting from the replacement of H by H_0 [the latter being defined as the first term of the rhs of (2.1)]. It then follows that, to obtain the contribution proportional to J^3, the operators $e^{-H(\beta-u)}$ and e^{-uH} need only be developed to first order in $\langle n_j|V_{ji}{}^{(H)}|n_i\rangle$.

Following the standard procedure, one notes that e^{-uH} obeys the so-called Bloch equation

$$(d/du)e^{-uH}=-He^{-uH}. \tag{3.6}$$

[14] The proof is straightforward. If one works in the "undisplaced lattice-coordinate" representation $\Phi_i(\mathbf{r})\pi_\lambda\chi_{N\lambda}(Q_\lambda)$ one deals with matrix elements $\langle j,n_j|\mathbf{r}^{(2)}|i,n_i\rangle=\langle j|\mathbf{r}^{(2)}|i\rangle\delta_{n_i,n_j}$ which are diagonal in, and independent of, the lattice quantum-numbers N_λ (as in standard tight-binding theory). For a periodic arrangement of sites, the eigenvalues of $\mathbf{r}^{(2)}$ are obtained immediately; they are $\mathbf{r}^{(2)}(\mathbf{k})=\sum_j e^{i\mathbf{k}\cdot\mathbf{R}_{ij}}\langle j|\mathbf{r}^{(2)}|i\rangle$ (where $\mathbf{k}$ is a reduced wave vector of the reciprocal lattice). The $r^{(2)}(\mathbf{k})$ are manifestly bounded; in fact, it is readily shown that $|\mathbf{r}^{(2)}(\mathbf{k})|\sim(eHa^3/\hbar c)S_{ji}$, where a is an interatomic distance and S_{ji} the overlap parameter [cf. Eq. (A12)].

[15] Strictly speaking, these "third-order" contributions are actually of first order in S_{ji} and second order in the charge-transfer parameter J_{ji} [defined as the zero-field limit of Eq. (A13) of Appendix A], i.e., they are $\propto S_{ji}J_{ji}{}^2$. The statement in the text implicity presupposes the simplification of regarding J_{ji} as proportional to S_{ji}. Such a simplification is in fact appropriate for the standard case of s-type local-site functions, as well as for the two-dimensional molecular-crystal model of FH, in which the magnitudes of both J_{ji} and S_{ji} are determined principally by an exponential factor of the form e^{-R_{ji}/R_0}, describing the overlap of the local-site functions. It is in this sense that terms, actually proportional to $S_{ji}J_{ji}{}^2$, are labeled as "third order in S_{ji}" [and hence to be compared with the *nonvanishing* contributions to μ_{xy} of third order in J_{ji}, obtained, both in FH and in the present paper, within the framework of the "site" approximation (2.6)]. Finally, with respect to higher orders, an "nth-order" term is actually $\propto S_{ji}J_{ji}{}^{n-1}$.

Introducing the substitution

$$e^{-uH}=e^{-uH_0}S(u) \tag{3.7}$$

into (3.6), one has for $S(u)$ the equation

$$dS(u)/du=-H'(u)S(u)\,, \tag{3.8}$$

where

$$H'(u)\equiv e^{uH_0}H_1e^{-uH_0} \tag{3.9}$$

and H_1 denotes the operator whose matrix elements are $\langle n_j|V_{ji}^{(H)}|i\rangle$. Furthermore, it is readily seen that, at $u=0$, $S(u)$ satisfies the initial-value condition[16]

$$S(0)=1. \tag{3.10}$$

One then iteratively integrates (3.8), obtaining

$$S(u)=1-\int_0^u e^{u'H_0}H_1e^{-u'H_0}du'$$

or, in matrix notation,

$$\langle jn_j|S|in_i\rangle=\delta_{ij}\delta_{n_in_j}$$
$$-\int_0^u e^{u'[\epsilon_j(n_j)-\epsilon_i(n_i)]}\langle n_j|V_{ji}^{(H)}|n_i\rangle du'$$
$$=\delta_{ij}\delta_{n_in_j}-\langle n_j|V_{ji}^{(H)}|n_i\rangle\left[\frac{e^{u[\epsilon_j(n_j)-\epsilon_i(n_i)]}-1}{\epsilon_j(n_j)-\epsilon_i(n_i)}\right]. \tag{3.11}$$

Bearing in mind that

$$\langle jn_j|e^{-uH_0}|in_i\rangle=\delta_{ij}\delta_{n_in_j}e^{-u\epsilon_i(n_i)}\,,$$

one has, to the required order in J,

$$jn_j|e^{-uH}|in_i\rangle=\delta_{ij}\delta_{n_in_j}$$
$$\times e^{-u\epsilon_i(n_i)}+\frac{e^{-u\epsilon_j(n_j)}-e^{-u\epsilon_i(n_i)}}{\epsilon_j(n_j)-\epsilon_i(n_i)}\langle n_j|V_{ji}^{(H)}|n_i\rangle. \tag{3.12}$$

One now substitutes (3.12), together with the completely analogous relationship for the operator $e^{-H(\beta-u)}$ into (3.3), and obtains (in the $|i,n_i\rangle$ representation)

$$\mathfrak{F}_{xy}(\hbar\omega_r)=\frac{1}{Z}\sum_{\substack{ijk\\ n_in_jn_k}}\int_0^\beta e^{\hbar\omega_r u}\{e^{-\epsilon_i(n_i)(\beta-u)}\langle in_i|v_x|jn_j\rangle$$
$$\times\langle n_j|V_{jk}^{(H)}|n_k\rangle\left(\frac{e^{-u\epsilon_j(n_j)}-e^{-u\epsilon_k(n_k)}}{\epsilon_j(n_j)-\epsilon_k(n_k)}\right)\langle kn_k|v_y|in_i\rangle$$
$$+\left(\frac{e^{-(\beta-u)\epsilon_i(n_i)}-e^{-(\beta-u)\epsilon_j(n_j)}}{\epsilon_i(n_i)-\epsilon_j(n_j)}\right)\langle n_i|V_{ij}^{(H)}|n_j\rangle$$
$$\times\langle jn_j|v_x|kn_k\rangle e^{-u\epsilon_k(n_k)}\langle kn_k|v_y|in_i\rangle\}du. \tag{3.13}$$

Carrying out the u integration, making use of the relationship

$$e^{\hbar\omega_r\beta}=1$$

which holds by virtue of (3.4), and replacing ω_r by Ω/h [that is, analytically continuing $\mathfrak{F}_{xy}(\hbar\omega_r)$ to the region immediately above the real axis in the ω plane], one has

$$\mathfrak{F}_{xy}(\Omega)=\frac{1}{Z}\sum_{\substack{ijk\\ n_in_jn_k}}\left[\left(\frac{e^{-\beta\epsilon_j}-e^{-\beta\epsilon_i}}{\Omega+\epsilon_i-\epsilon_j}-\frac{e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i}}{\Omega+\epsilon_i-\epsilon_k}\right)\right.$$
$$\times\frac{\langle i|v_x|j\rangle V_{jk}^{(H)}\langle k|v_y|i\rangle}{\epsilon_j-\epsilon_k}+\left(\frac{e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i}}{\Omega+\epsilon_i-\epsilon_k}\right.$$
$$\left.\left.-\frac{e^{-\beta\epsilon_k}-e^{-\beta\epsilon_j}}{\Omega+\epsilon_j-\epsilon_k}\right)\frac{V_{ij}^{(H)}\langle j|v_x|k\rangle\langle k|v_y|i\rangle}{\epsilon_i-\epsilon_j}\right], \tag{3.14}$$

wherein the notational simplification of dropping the indices n_i, etc., in the energies and matrix elements has been introduced; i.e.,

$$\epsilon_i(n_i)\longrightarrow\epsilon_i\,, \tag{3.15a}$$

$$\langle in_i|\mathbf{v}|jn_j\rangle\longrightarrow\langle i|\mathbf{v}|j\rangle\,, \tag{3.15b}$$

$$\langle n_j|V_{jk}^{(H)}|n_k\rangle\longrightarrow V_{jk}^{(H)}. \tag{3.15c}$$

It is now of interest to write down an expression for the antisymmetric component of the correlation-function tensor

$$\mathfrak{F}_{xy}^{(a)}(\Omega)\equiv\tfrac{1}{2}[\mathfrak{F}_{xy}(\Omega)-\mathfrak{F}_{yx}(\Omega)]. \tag{3.16}$$

This component, when inserted into (3.2), yields directly the antisymmetric part of the conductivity tensor, $\sigma_{xy}^{(a)}\equiv\frac{1}{2}(\sigma_{xy}-\sigma_{yx})$; as may be seen from Onsager's general relationship,[17]

$$\sigma_{xy}(H)=\sigma_{yx}(-H)\,,$$

$\sigma_{xy}^{(a)}$ is odd in the magnetic field, and is hence the relevant conductivity for the dc Hall effect.

One inserts (3.14) into (3.16)—or, more expeditiously, the expression which is gotten from (3.14) by a cyclic permutation of the indices i, j, k of its *second term* (i.e., $i\to j$, $j\to k$, $k\to i$); also, of course, $n_i\to n_j$, $n_j\to n_k$, $n_k\to n_i$, the summation $\sum_{ijkn_in_jn_k}$ in front of (3.14) being invariant to such a permutation; the result is

$$\mathfrak{F}_{xy}^{(a)}(\Omega)=\frac{1}{Z}\sum_{\substack{ijk\\ n_in_jn_k}}\Omega V_{jk}^{(H)}\{\langle k|v_x|i\rangle\langle i|v_y|j\rangle$$
$$-\langle k|v_y|i\rangle\langle i|v_x|j\rangle\}g_{jk;i}\,, \tag{3.17}$$

where

$$g_{kj;i}\equiv\frac{1}{\epsilon_j-\epsilon_k}\left[\frac{e^{-\beta\epsilon_j}-e^{-\beta\epsilon_i}}{(\epsilon_j-\epsilon_i)^2-\Omega^2}\right.$$
$$\left.-\frac{e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i}}{(\epsilon_k-\epsilon_i)^2-\Omega^2}\right]=g_{jk;i}. \tag{3.18}$$

[16] Note that e^{-uH} and e^{-uH_0} both reduce to unity at $u=0$.

[17] Refer to, e.g., R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957), especially Eq. (6.9).

The next (obvious) step is the elimination of the velocity matrix elements in (3.18) by the use of (2.7). One obtains

$$\mathfrak{F}_{xy}{}^{(a)}(\Omega)=-\frac{2\Omega}{Z\hbar^2}\sum_{\substack{ijk\\ninjnk}} V_{jk}{}^{(H)}V_{ki}{}^{(H)}V_{ij}{}^{H}A_{kji}{}^{(Z)}g_{jk;i}, \tag{3.19}$$

where [cf. Eq. (A19) of Appendix A] $A_{kji}{}^{(Z)}$ is the z component of the (vector) area of the triangle subtended by the sites i, j, k.

At this stage, it is desirable to utilize an additional symmetry property of (3.19)—namely, its invariance with respect to interchange of the indices, j and k (said interchange implying a corresponding interchange of the indices, n_j and n_k). Noting that $g_{jk;i}$ is symmetric, whereas $\mathbf{A}_{kji}$ is antisymmetric, with respect to interchange of the indices j and k, one may cast (3.19) in a form which differs from the original solely in the replacement,

$$\begin{aligned}&V_{jk}{}^{(H)}V_{ki}{}^{(H)}V_{ij}{}^{(H)}\rightarrow\\ &\tfrac{1}{2}(V_{jk}{}^{(H)}V_{ki}{}^{(H)}V_{ij}{}^{(H)}-V_{kj}{}^{(H)}V_{ji}{}^{(H)}V_{ik}{}^{(H)})\\ &=\tfrac{1}{2}[V_{jk}{}^{(H)}V_{ki}{}^{(H)}V_{ij}{}^{(H)}-(V_{jk}{}^{(H)}V_{ki}{}^{(H)}V_{ij}{}^{(H)})^*]\\ &=iV_{jk}V_{ki}V_{ij}\sin(\alpha_{jk}+\alpha_{ki}+\alpha_{ij})\\ &=iV_{jk}V_{ki}V_{ij}\sin(e\mathbf{H}\cdot\mathbf{A}_{kji}/\hbar c),\end{aligned} \tag{3.20}$$

where V_{jk}, etc., are the zero-field values of the transfer matrix elements; in obtaining the equalities of (3.20), successive use has been made of (a) the Hermiticity of the $V_{ij}{}^{(H)}$, (b) Eqs. (2.1) and (2.4), and (c) the basic flux-relation (2.3) [together with the obvious one, $\alpha_{ij}=-\alpha_{ji}$, etc., which follows from (2.3), (2.4), and the Hermiticity of the $V_{ij}{}^{(H)}$].

It should at this point be noted that (2.2) has actually been derived only to first order in the magnetic field. In view of this circumstance, the replacement

$$\sin(e\mathbf{H}\cdot\mathbf{A}_{kji}/\hbar c)\rightarrow e\mathbf{H}\cdot\mathbf{A}_{kji}/\hbar c$$

will be used throughout in what follows. Then, upon inserting (3.20) into (3.19), one has

$$\mathfrak{F}_{xy}{}^{(a)}(\Omega)=-\frac{2\Omega ieH}{Z\hbar^3C}\times\sum_{\substack{ijk\\npnjnk}} V_{jk}V_{ki}V_{ij}(A_{kji}{}^{(Z)})^2g_{jk;i}. \tag{3.21}$$

Turning, now, to the further evaluation of $g_{jk;i}$, one may (after a little algebra) rewrite (3.18) in the form

$$g_{jk;i}=g_{jk;i}{}^{(1)}+g_{jk;i}{}^{(2)}, \tag{3.22}$$

where

$$g_{jk;i}{}^{(1)}=\Omega^2\left(\frac{e^{-\beta\epsilon_k}-e^{-\beta\epsilon_j}}{\epsilon_j-\epsilon_k}\right)\frac{1}{[(\epsilon_j-\epsilon_i)^2-\Omega^2][(\epsilon_k-\epsilon_i)^2-\Omega^2]} \tag{3.23}$$

and

$$g_{jk;i}{}^{(2)}=\frac{1}{\epsilon_j-\epsilon_k}\left\{\frac{(e^{-\beta\epsilon_j}-e^{-\beta\epsilon_i})(\epsilon_k-\epsilon_i)^2-(e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i})(\epsilon_j-\epsilon_i)^2}{[(\epsilon_j-\epsilon_i)^2-\Omega^2][(\epsilon_k-\epsilon_i)^2-\Omega^2]}\right\}=g_{jk;i}{}^{(2a)}+g_{jk;i}{}^{(2b)}, \tag{3.24}$$

where

$$g_{jk;i}{}^{(2a)}=-\frac{\Omega^2}{\epsilon_j-\epsilon_k}\left\{\frac{(e^{-\beta\epsilon_j}-e^{-\beta\epsilon_i})(\epsilon_k-\epsilon_i)^2-(e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i})(\epsilon_j-\epsilon_i)}{[(\epsilon_j-\epsilon_k)^2-\Omega^2][(\epsilon_j-\epsilon_i)^2-\Omega^2][(\epsilon_k-\epsilon_i)^2-\Omega^2]}\right\} \tag{3.25}$$

and

$$g_{jk;i}{}^{(2b)}=\frac{(e^{-\beta\epsilon_j}-e^{-\beta\epsilon_i})(\epsilon_k-\epsilon_i)^2(\epsilon_j-\epsilon_k)-(e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i})(\epsilon_j-\epsilon_i)^2(\epsilon_j-\epsilon_k)}{[(\epsilon_j-\epsilon_i)^2-\Omega^2][(\epsilon_j-\epsilon_k)^2-\Omega^2][(\epsilon_k-\epsilon_i)^2-\Omega^2]}. \tag{3.26}$$

In what follows, it will be demonstrated that (1) $g_{jk;i}{}^{(2b)}$ makes no contribution to $\mathfrak{F}_{xy}{}^{(a)}(\Omega)$, and (2) in the limit of sufficiently small Ω (i.e., the dc case), the dependence of $g_{jk;i}{}^{(1)}$ and $g_{jk;i}{}^{(2a)}$ on the local-site energies ϵ_i, ϵ_j, and ϵ_k is of the form,[18] $e^{-\beta\epsilon_i}\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i)$.

(1) To prove that $g_{jk;i}{}^{(2b)}$ yields no contribution to (3.21), let us note that (a) the rhs of (3.21) is invariant with respect to a permutation of the summation indices, $i(n_i)$, $j(n_j)$, $k(n_k)$; moreover, the factor of $g_{jk;i}$, namely, $V_{jk}V_{ki}V_{ij}(A_{kji}{}^{(Z)})^2$, is manifestly invariant towards such a permutation. It therefore follows that the replacement of $g_{jk;i}$, or what is of interest here, $g_{jk;i}{}^{(2b)}$, by its cyclic average, i.e.,

$$g_{jk;i}{}^{(2b)}\rightarrow\tfrac{1}{3}[g_{jk;i}{}^{(2b)}+g_{ki;j}{}^{(2b)}+g_{ij;k}{}^{(2b)}] \tag{3.27}$$

is permissible. Let us now couple the first term of $g_{jk;i}{}^{(2b)}$ with the second term of $g_{ki;j}{}^{(2b)}$. One thereby obtains an expression, the numerator[19] of which is

$$\begin{aligned}&(e^{-\beta\epsilon_j}-e^{-\beta\epsilon_i})(\epsilon_k-\epsilon_i)^2(\epsilon_j-\epsilon_k)\\ &\quad-(e^{-\beta\epsilon_i}-e^{-\beta\epsilon_j})(\epsilon_k-\epsilon_j)^2(\epsilon_k-\epsilon_i)\\ &\quad=-(e^{-\beta\epsilon_j}-e^{-\beta\epsilon_i})(\epsilon_k-\epsilon_i)(\epsilon_j-\epsilon_k)(\epsilon_k-\epsilon_j).\end{aligned}$$

If one now adds to this expression the numerators of the other two such terms—namely, the first term of $g_{ki;j}{}^{(2b)}$ plus the second of $g_{ij;k}{}^{(2b)}$, and the first term of $g_{ij;k}{}^{(2b)}$ plus the second of $g_{jk;i}{}^{(2b)}$—one readily verifies that the resultant sum is zero, Q.E.D.

[18] Note that this δ-function dependence on relative local-site energies is precisely of the type exhibited in the expression for the field-dependent part of the jump-probability $\omega_3{}^{(H)}$ on the bottom of p. 515 of FH.

[19] The denominator, consisting of the three square brackets of (3.26), is manifestly invariant with respect to cyclic permutations, and is thus a common factor of all the terms in (3.27).

(2a) The limit of $\mathcal{J}_{jk;i}^{(1)}$ as $\Omega \to 0$: To begin, let us note that $\mathcal{J}_{jk;i}^{(1)}$ enters into a sum over the lattice quantum numbers n_i, n_j, n_k and that, in such a sum, the energies ϵ_i, ϵ_j, and ϵ_k each range over a continuous spectrum. It is then immediately apparent that, as $\Omega \to 0$, the factor Ω^2 in the numerator of (3.23) will cause the expression to vanish unless it gets compensated by singularities (or resonances) in the energy denominators occurring in the vicinity of the "energy coincidences"[20] $\epsilon_i = \epsilon_j$, $\epsilon_i = \epsilon_k$, or $\epsilon_j = \epsilon_k$. In particular, as will now be shown, the only nonvanishing contributions to the summation (over the n_i, n_j, n_k) occur in the vicinity of "triple coincidences," in which $|\epsilon_i - \epsilon_j| \sim |\epsilon_i - \epsilon_k| \sim \Omega$.

To prove the above statement, let us restrict the n_i, n_j, n_k summation to regions which satisfy the inequality $|\epsilon_j - \epsilon_k| \gg \Omega$. It is then clear that the only resonances which have to be considered are those of the square-bracketed factors in the denominator of (3.23), occurring at $\epsilon_i = \epsilon_j$ and $\epsilon_i = \epsilon_k$; by virtue of the condition $|\epsilon_j - \epsilon_k| \gg \Omega$, these are nonoverlapping—i.e., in the integration over the resonance region of one of them, the other may be considered as constant. In an integration, e.g., over the n_i—in which ϵ_i sweeps out its spectral range—one encounters integrals of the type

$$\int_{-\infty}^{+\infty} \frac{dx}{x^2-\Omega^2} = \int_{-\infty}^{+\infty} \frac{dx}{(x-\Omega)(x+\Omega)} = \frac{\pi i}{\Omega},$$

the factor Ω^{-1} resulting from such integrations is not sufficient to cancel the factor Ω^2 in the numerator of (3.23). It is thus apparent that the only possible source of a nonvanishing contribution is the triple-coincidence region, $|\epsilon_i - \epsilon_j| \sim |\epsilon_i - \epsilon_k| \sim \Omega$. For this region, the replacement

$$\frac{e^{-\beta\epsilon_k} - e^{-\beta\epsilon_j}}{\epsilon_j - \epsilon_k} \to \beta e^{-\beta\epsilon_j}$$

becomes appropriate; moreover, the restriction to the triple-coincidence region means that, in effect (i.e., formally) each square bracket in the denominator of (3.23) may be replaced by $\pi i/\Omega$ times the appropriate delta function,[21] e.g.,

$$\frac{1}{[(\epsilon_j-\epsilon_i)^2-\Omega^2]} \to \frac{\pi i}{\Omega}\delta(\epsilon_j-\epsilon_i). \qquad (3.28)$$

[20] It should be stated that no such singularities occur in the factors of (3.21), that is, neither in the V_{ij}'s nor in $A_{kji}^{(Z)}$. [An exception to this statement is the "zero-phonon" term in V_{ij}, which occurs for the case of *exact resonance* (or, in the language of FH, the "diagonal transitions"), when all the n_i equal all the n_j or n_k; such transitions may be excluded either by FH's subtraction technique or, if one desires greater sophistication, by a resolvent, density-matrix, or correlation-function technique in which lifetime damping is taken into account by the infinite selective summation of appropriate terms. The universal result of all the published theoretical works is that, in the hopping regime, the diagonal transitions are unimportant; they will hence be ignored in the present paper.]

[21] The integrations over the two square brackets are to be considered as mutually independent. Namely, one may fix the n_i and sum over the n_j and n_k; such a summation is equivalent to integrating over ϵ_j and δ_k independently.

Introducing replacements of this type into (3.23), one has

$$\mathcal{J}_{jk;i}^{(1)} \xrightarrow{\Omega\to 0} -\beta e^{-\beta\epsilon_i}\pi^2\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i). \qquad (3.29)$$

(2b) With respect to the term $\mathcal{J}_{jk;i}^{(2a)}$ [given by (3.25)], let us first establish that, similar to the case for $\mathcal{J}_{jk;i}^{(1)}$, its principal contribution to the sum in (3.21) occurs in the triple-coincidence region,

$$|\epsilon_i-\epsilon_j| \sim |\epsilon_i-\epsilon_k| \sim |\Omega|.$$

To this end, let us write the rhs of (3.25) as a sum of the two terms,

$$-\frac{\Omega^2}{\epsilon_j-\epsilon_k}\left\{\frac{(\frac{1}{2}e^{-\beta\epsilon_j}+\frac{1}{2}e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i})[(\epsilon_k-\epsilon_i)^2-(\epsilon_j-\epsilon_i)^2]}{[\cdots][\cdots][\cdots]}\right\}$$

$$=-\Omega^2\left\{\frac{(\frac{1}{2}e^{-\beta\epsilon_j}+\frac{1}{2}e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i})(\epsilon_k+\epsilon_j-2\epsilon_i)}{[(\epsilon_j-\epsilon_k)^2-\Omega^2][(\epsilon_j-\epsilon_i)^2-\Omega^2][(\epsilon_k-\epsilon_i)^2-\Omega^2]}\right\}$$

and

$$-\left(\frac{\Omega^2}{2}\right)\left(\frac{e^{-\beta\epsilon_j}-e^{-\beta\epsilon_k}}{\epsilon_j-\epsilon_k}\right)$$

$$\times\frac{(\epsilon_k-\epsilon_i)^2+(\epsilon_j-\epsilon_i)^2}{([\epsilon_k-\epsilon_j)^2-\Omega^2][(\epsilon_j-\epsilon_i)^2-\Omega^2][(\epsilon_k-\epsilon_i)^2-\Omega^2]}.$$

It is to be noted that, in each of these terms, there occur no denominator singularities except those associated with the passage to the limit $\Omega \to 0$. One may then apply the same procedure as was used above for $\mathcal{J}_{jk;i}^{(1)}$ to establish that, when the n_i, n_j, n_k summation is limited by the restriction that, e.g., $|\epsilon_j-\epsilon_k| \gg |\Omega|$, the contribution to (3.21) vanishes in the limit $\Omega \to 0$. Namely, as before, the only singular regions are $|\epsilon_i-\epsilon_j| \sim |\Omega|$ and $|\epsilon_i-\epsilon_k| \sim |\Omega|$, at which the second and third denominator brackets in both terms of $\mathcal{J}_{jk;i}^{(2a)}$ produce (nonoverlapping) resonances. Summing over n_i (or equivalently, integrating over ϵ_i), one obtains, e.g., from the region $|\epsilon_i-\epsilon_j| \sim |\Omega|$, contributions of the form $(\pi i/\Omega) \times (1/(\epsilon_j-\epsilon_i)^4) \times$ nonsingular, Ω-independent factors; similar expressions are obtained from the region $|\epsilon_i-\epsilon_k| \sim |\Omega|$. It is then seen that, subject to the condition $|\epsilon_j-\epsilon_k| \gg |\Omega|$, there are no further singularities capable of producing additional factors of Ω^{-1}; the net Ω dependence is then simply $\sim\Omega$, which vanishes as $\Omega \to 0$, Q.E.D.

From the above discussion it then follows that one may introduce into (3.21) the replacement

$$\mathcal{J}_{jk;i}^{(2a)} \to A\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i), \qquad (3.30)$$

where

$$A \equiv \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathcal{J}_{jk;i}^{(2a)} d(\epsilon_j-\epsilon_i) d(\epsilon_k-\epsilon_i) \qquad (3.31)$$

is (by definition) the appropriate normalizing factor.

For the integrand of (3.31), it is expedient to insert the rhs of (3.25)—with, however, the replacements

$$(e^{-\beta\epsilon_j}-e^{-\beta\epsilon_i})\rightarrow-\beta e^{-\beta\epsilon_i}(\epsilon_j-\epsilon_i)$$

and

$$(e^{-\beta\epsilon_k}-e^{-\beta\epsilon_i})\rightarrow-\beta e^{-\beta\epsilon_i}(\epsilon_k-\epsilon_i)$$

which are valid in the triple-coincidence region. One thereby has

$$A=\Omega^2 e^{-\beta\epsilon_i}\int_{-\infty}^{+\infty}dx\int_{-\infty}^{+\infty}dy\times\frac{xy}{[x^2-\Omega^2][y^2-\Omega^2][(x-y)^2-\Omega^2]}$$

which, with the introduction of the Dirichlet representation of the delta function, can be written as

$$A=\frac{\Omega^2\beta e^{-\beta\epsilon_i}}{2\pi}\int_{-\infty}^{+\infty}d\alpha\times\int\int\int_{-\infty}^{+\infty}\frac{xye^{i\alpha(y+z-x)}dxdydz}{[x^2-\Omega^2][y^2-\Omega^2][z^2-\Omega^2]}.$$

The x, y, z integrations factor; the individual integrals being of standard form, one obtains (with $\mathrm{Im}\Omega\equiv\hbar s>0$)

$$A=\frac{i\pi^3\Omega\beta e^{-\beta\epsilon_i}}{2\pi}\int_{-\infty}^{+\infty}e^{3i|\alpha|\Omega}d\alpha=\frac{\pi^2}{2}\beta e^{-\beta\epsilon_i}. \quad (3.32)$$

Inserting (3.32) into (3.30), one has

$$\mathcal{J}_{jk;i}^{(2a)}\overset{\Omega\rightarrow0}{\rightarrow}\frac{\pi^2}{3}\beta e^{-\beta\epsilon_i}\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i)$$

which, when combined with (3.29), yields for the total $\mathcal{J}_{jk;i}$ the replacement

$$\mathcal{J}_{jk;i}\overset{\Omega\rightarrow0}{\rightarrow}\frac{2\pi^2}{3}\beta e^{-\beta\epsilon_i}\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i); \quad (3.33)$$

when this replacement is inserted into (3.21), one has

$$\mathfrak{F}_{xy}^{(a)}(\Omega)\overset{\Omega\rightarrow0}{\rightarrow}\frac{4\Omega ieH}{3Z\hbar^3c}\beta\pi^2\sum_{\substack{ijk\\ n_i n_j n_k}}\frac{1}{\hbar}V_{jk}V_{ki}V_{ij}\times e^{-\beta\epsilon_i}\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i). \quad (3.34)$$

Equation (3.34) may now be introduced into (3.2); the result is [cf. (3.1) and (3.16)]

$$\sigma_{xy}^{(a)}(0)=+\frac{4\pi^2\beta e^2}{3ZV}\left(\frac{eH}{\hbar c}A_{kji}^{(Z)}\right)A_{kji}^{(Z)}\times\sum_{\substack{ijk\\ n_i n_j n_k}}\frac{1}{\hbar}V_{jk}V_{ki}V_{ij}E^{-\beta\epsilon_i}\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i). \quad (3.35)$$

It now remains to be shown that (3.35) is derivable from the basic three-site transition-probability expression of FH. This expression (the last equation on p. 515 of FH), when transcribed in terms of the notation of the present paper, reads [cf. Appendix equation (A18)]

$$\omega_3^{(H)}(ijk)=-\left(\frac{eH}{\hbar c}A_{kji}^{(Z)}\right)\frac{4\pi^2}{\hbar}\sum_{n_j n_k}V_{jk}V_{ki}V_{ij}\times\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i). \quad (3.36)$$

In writing down (3.36), the argument "ijk" has been attached to $\omega_3^{(H)}$; the order indicates that the transition in question is from site i to site k, via the intermediate site j. Stated more explicitly, (3.36) gives the magnetic-field-dependent part of the probability that, starting from a particular state in which the charge carrier is on site i, and in which the vibration quantum numbers n_i are specified, a transition occurs to site k, without regard for the final vibration quantum numbers n_k; this transition furthermore incorporates the effect of interference between the amplitude for the direct ($i\rightarrow k$) transition and that for the two-stage amplitude, in which the intermediate state is specified with respect to its site variable j but in which the sum is taken over all possible intermediate vibration quantum numbers n_j.

Following the procedure of FH (contained mainly in Sec. 4 of that paper)[22] one goes over to the thermal average of $\omega_3^{(H)}$ (with respect to the initial vibrational quantum numbers n_i). This quantity is

$$\langle\omega_3^{(H)}(ijk)\rangle=\frac{1}{Z_i}\sum_{n_i}e^{-\beta\epsilon_i(n_i)}\omega_3^{(H)}(ijk), \quad (3.37)$$

where

$$Z_i=\sum_{n_i}e^{-\beta\epsilon_i(n_i)} \quad (3.38)$$

is the "uni-site" partition function, i.e., the partition function calculated with the restriction that the charge carrier be localized at a particular (ith) site.

A general expression for the Hall-current density in hopping-type charge transport reads[23]

[22] The treatment given here is in fact but a generalization of that of FH's Sec. 4 to an arbitrary lattice structure. It should be pointed out that its first step, namely the averaging of $\omega_3^{(H)}$ over the initial lattice quantum numbers, n_i (cf. FH, bottom of p. 517), may be justified *a priori*, without recourse to a polaron transport equation. The reason is, in essence, that, in a system containing a single charge carrier, the transport dynamics of said charge carrier can scarcely disturb the equilibrium of an infinite number of phonon modes. More specifically, such equilibrium is achieved via internal phonon-phonon interactions [not explicitly included in the original lattice Hamiltonian, as given by the quadratic form (A25)], and by interactions with the "external world" (e.g., via boundaries). In comparison with such interactions, the equilibrium-perturbing effect of the single charge carrier is smaller by a factor of the order of the number of unit cells in the sample, and hence entirely negligible.

[23] Equation (3.39) is a straightforward expression of magnetic-field-dependent rate of charge displacement per unit volume due to elementary site-jumps, i.e., that part of the total rate which depends linearly on the magnetic field.

$$\mathbf{j}^{(H)}=-\frac{e}{V}\sum_{ijk}\langle W_3{}^{(H)}(ijk)\rangle\mathbf{R}_{ki}f_i, \tag{3.39}$$

where f_i is the probability of occupancy of site i.

In principle, f_i would have to be determined by solving a transport equation in site-variable space, in which $\omega_3{}^{(H)}(ijk)$ (together, of course, with the zeroth-order, magnetic-field-independent hopping rate) describes the elementary transition process. For a spatially uniform system, however, it is known that, for the steady-state situation, the distribution of carriers must be spatially uniform, i.e.,

$$f_i=1/N, \tag{3.40}$$

where N is the number of sites in the sample; in the absence of an electric field

$$N=Z/Z_i. \tag{3.41}$$

Inserting (3.40) and (3.37) into (3.39), one has

$$\mathbf{j}^{(H)}=-\frac{e}{NV}\sum_{\substack{ijk\\ni}}\frac{1}{Z_i}e^{-\beta\epsilon_i(n_i)}\omega_3{}^{(H)}(ijk)\mathbf{R}_{ki}. \tag{3.42}$$

At this point, it is expedient to take explicit account of the external electric field. In a hopping model, the primary effect of a field $\mathcal{E}$ is to modify the local-site energies, according to the formula

$$\epsilon_i(n_i)=\epsilon_i{}^{(0)}(n_i)+e\mathcal{E}\cdot\mathbf{R}_i, \tag{3.43}$$

where $\epsilon_i{}^{(0)}(n_i)$ denotes the value of $\epsilon_i(n_i)$ for $\mathcal{E}=0$. Let us note that the local partition function thereby undergoes the modification

$$Z_i\rightarrow Z_ie^{-\beta e\mathcal{E}\cdot\mathbf{R}_i} \tag{3.44}$$

(Z_i now denoting the zero-field local partition function). Upon inserting (3.43), (3.44), and (3.36) into (3.42), one has [upon eliminating N via the use of (3.41)]

$$\mathbf{j}^{(H)}=\frac{e}{VZ}\sum_{\substack{ijk\\ninjnk}}e^{-\beta\epsilon_i}(1+\beta e\mathcal{E}\cdot\mathbf{R}_i)\mathbf{R}_{ki}\left(\frac{eHA_{kji}{}^{(Z)}}{\hbar c}\right)\frac{4\pi^2}{\hbar}$$
$$\times V_{jk}V_{ki}V_{ij}\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i), \tag{3.45}$$

where the notation defined by (3.15a) has been introduced, and where the fact that $\mathcal{E}$ is infinitesimal has been utilized to expand the exponential factor in (3.44).

One now replaces the rhs of (3.45) by its "cyclic average," i.e., by $\frac{1}{3}$ the sum of the rhs plus two other terms gotten by cyclically permuting the site indices i, j, k (as well as n_i, n_j, n_k). In carrying out this permutation, one utilizes the relation $\epsilon_i=\epsilon_j=\epsilon_k$ contained in the energy-conserving delta functions, to replace $e^{-\beta\epsilon_j}$ and $e^{-\beta\epsilon_k}$ by $e^{-\beta\epsilon_i}$, thereby obtaining

$$\mathbf{j}^{(H)}=\frac{4\pi^2e}{3VZ\hbar}\sum_{\substack{ijk\\ninjnk}}e^{-\beta\epsilon_i}\left(\frac{eHA_{kji}{}^{(Z)}}{\hbar c}\right)V_{jk}V_{ki}V_{ij}$$
$$\times\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i)\{\mathbf{R}_{ki}+\mathbf{R}_{ij}+\mathbf{R}_{jk}$$
$$+\beta e\mathcal{E}\cdot[\mathbf{R}_i\mathbf{R}_{ki}+\mathbf{R}_j\mathbf{R}_{ij}+\mathbf{R}_k\mathbf{R}_{jk}]\}.$$

Let us now note that the field-independent term in the curly bracket vanishes (as it must), so that $\mathbf{j}^{(H)}$ is proportional to the external field. The associated conductivity tensor is

$$\sigma_{xy}=\frac{4\pi^2\beta e^2}{3VZ\hbar}\sum_{\substack{ijk\\ninjnk}}e^{-\beta\epsilon_i}\left(\frac{eHA_{kji}{}^{(Z)}}{\hbar c}\right)V_{jk}V_{ki}V_{ij}$$
$$\times\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i)[X_{ki}Y_i+X_{ij}Y_j+X_{jk}Y_k]. \tag{3.46}$$

For the comparison with (3.35), one seeks the antisymmetric part of (3.46); carrying out the antisymmetrization, and using geometrical relationships of the form

$$\mathbf{R}_{jk}=\mathbf{R}_j-\mathbf{R}_i=\mathbf{R}_{ji}+\mathbf{R}_{ij}=-\mathbf{R}_{ij}-\mathbf{R}_{ki},$$

one obtains

$$\sigma_{xy}{}^{(a)}=\frac{2}{3}\frac{\pi^2\beta e^2}{VZ\hbar}\sum_{\substack{ijk\\ninjnk}}e^{-\beta\epsilon_i}\left(\frac{eHA_{kji}{}^{(Z)}}{\hbar c}\right)V_{jk}V_{ki}V_{ij}$$
$$\times\delta(\epsilon_j-\epsilon_i)\delta(\epsilon_k-\epsilon_i)[X_{ki}Y_{ij}-Y_{ki}X_{ij}]$$

which, by virtue of the Appendix equation (A19), the z component of which reads

$$2A_{kji}{}^{(Z)}=X_{ji}Y_{ki}-Y_{ji}X_{ki}=X_{ki}Y_{ij}-Y_{ki}X_{ij}$$

is seen to coincide with (3.35), Q.E.D.

Further remarks: The preceding treatment has established the equivalence between the Kubo formulation and the jump-probability approach of FH [as embodied in Eq. (2.36) of the present paper]. A reexamination of the detailed analysis of this equation in FH (FH, pp. 516–525, also Appendices C and D) has been carried out; only minor errata[24] were found. An auxiliary indication of the correctness of the calculation is the coincidence of the results with those of the *classical occurrence probability approach* of FH's Sec. II in the classical limit, $\hbar\omega_\lambda\ll\kappa T$, as expected.

APPENDIX A

The system of an excess electron (hole) in a host crystal will be described by a Hamiltonian of the general form

$$H=H_e+H_L+H_{\text{int}}, \tag{A1}$$

[24] These errata are herewith listed: (1) A factor of 2 should be inserted in front of the expression on the top of p. 519. (2) The integral in the middle of p. 521 should be multiplied by a factor $e^{-\alpha\beta\hbar/2}$.

that is, as a sum of terms describing (a) the motion of the excess electron (hole) in a rigid lattice, (b) the lattice vibrations, and (c) the interaction between the lattice vibrations and the charge carrier.

The electron (hole) Hamiltonian is chosen to have the form

$$H_e=(1/2m)[p+e\mathbf{A}/c]^2+\sum_i U(\mathbf{r}-\mathbf{R}_i) \quad \text{(A2)}$$

with $\mathbf{A}$ the vector-potential of the external magnetic field, expressed in the so-called "symmetric" gauge:

$$\mathbf{A}=\tfrac{1}{2}\mathbf{H}\times\mathbf{r}. \quad \text{(A3)}$$

In the spirit of the tight-binding approximation, one approximates the electron wave function by writing it as a superposition of local-site functions $\phi_i(\mathbf{r})$ which are eigenfunctions of "local-site" Hamiltonians

$$H_e^{(i)}\equiv(1/2m)(\mathbf{p}+e\mathbf{A}/c)^2+U(\mathbf{r}-\mathbf{R}_i), \quad \text{(A4)}$$

where $U(\mathbf{r}-\mathbf{R}_i)$ is an atomiclike potential, centered about $\mathbf{R}_i$, the center of symmetry of the ith site; each $\phi_i(\mathbf{r})$ is assumed to belong to a single nondegenerate energy level E_0. In the absence of the magnetic field, the $\phi_i(\mathbf{r})$ take the form

$$\phi_i(\mathbf{r})=u(\mathbf{r}-\mathbf{R}_i), \quad \text{(A5)}$$

the $u(\mathbf{r}-\mathbf{R}_i)$ may be taken as real without loss of generality. In the presence of the magnetic field, one conveniently introduces the gauge transformation

$$\phi_i(\mathbf{r})=e^{-ie(\mathbf{H}\times\mathbf{R}_i)\cdot\mathbf{r}/2\hbar c}u_i(\mathbf{r}) \quad \text{(A6)}$$

and notes that $u_i(\mathbf{r})$ obeys the equation

$$\left\{\frac{1}{2m}\left[p+\frac{e}{2c}H\times(\mathbf{r}-\mathbf{R}_i)\right]^2+U(\mathbf{r}-\mathbf{R}_i)\right\}u_i(\mathbf{r})=E_0u_i(\mathbf{r}) \quad \text{(A7)}$$

from which it is inferred that the functional dependence of $u_i(\mathbf{r})$ is of the form

$$u_i(\mathbf{r})=u^{(H)}(\mathbf{r}-\mathbf{R}_i).$$

[The superscript "(H)" denoting the fact that the quantities are field-dependent.] Furthermore, if the zero-field functions be taken as s states (or, more generally, as in the treatment of FH, cylindrically symmetric about the field direction), it is readily verified that, up to and including terms linear in the magnetic field, $u^{(H)}(\mathbf{r}-\mathbf{R}_i)$ is equal to its zero-field counterpart $u(\mathbf{r}-\mathbf{R}_i)$. Since the present paper is concerned only with linear effects, one may write

$$\phi_i(\mathbf{r})=e^{-ie(\mathbf{H}\times\mathbf{R}_i)\cdot\mathbf{r}/2\hbar c}u(\mathbf{r}-\mathbf{R}_i), \quad \text{(A8)}$$

wherein the field dependence is contained solely in the gauge factor.

Since the $\phi_i(\mathbf{r})$ are not in general orthogonal, it is technically convenient to introduce orthogonalized combinations $\Phi_i(\mathbf{r})$. A sufficiently accurate orthogonalization recipe is

$$\Phi_i(\mathbf{r})=\phi_i(\mathbf{r})-\tfrac{1}{2}\sum_{j\neq i}\phi_j(\mathbf{r})S_{ji}, \quad \text{(A9)}$$

where

$$S_{ji}\equiv\int\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})d^3\mathbf{r}=S_{ij}^* \quad \text{(A10)}$$

is the standard "overlap" integral of linear combination of atomic orbitals (LCAO) theory. The $\Phi_i(\mathbf{r})$ are orthogonal to first order in the overlap integral.

The full electronic Hamiltonian, as given by (A2) is now projected onto the subspace spanned by the $\Phi_i(\mathbf{r})$. In the representation of the $\Phi_i(\mathbf{r})$ one has

$$\langle j|H_e|i\rangle=(E_0+W_i)\delta_{ij}-J_{ji}^{(H)}(1-\delta_{ji}), \quad \text{(A11)}$$

where

$$W_i=\sum_{j\neq i}\int|\phi_i(\mathbf{r})|^2U_j(\mathbf{r}-\mathbf{R}_j)d^3r \quad \text{(A12)}$$

and

$$-J_{ji}^{(H)}=\int\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})\times[\sum_{k\neq i}U_k(\mathbf{r}-\mathbf{R}_k)]d^3r-\tfrac{1}{2}S_{ji}(W_i+W_j) \quad \text{(A13)}$$

[the superscript "(H)" denoting the fact that the quantities are field-dependent].

In a regular lattice of local-site vectors $\mathbf{R}_i$, the W_i are manifestly equal to one and the same constant. It is then convenient to choose the zero of energy so that E_0+W_i vanishes, and (A11) becomes

$$\langle j|H_e|i\rangle=-J_{ji}^{(H)}(1-\delta_{ji}). \quad \text{(A11')}$$

The field dependence of the $J_{ji}^{(H)}$ (which, as shown in FH, is crucial for the theory of the Hall effect in small-polaron theory—in fact, in any tight-binding theory) will now be discussed. Beginning with the second term of (A13), let us note [from (A8)] (a) that W_i does not depend on the field, and (b) the expression (A10) for S_{ji} may be written as

$$S_{ji}=\int u(\mathbf{r}-\mathbf{R}_i)u(\mathbf{r}-\mathbf{R}_j)e^{ie(\mathbf{H}\times\mathbf{R}_{ji})\cdot\mathbf{r}/2\hbar c}d^3r, \quad \text{(A10')}$$

where $\mathbf{R}_{ji}\equiv\mathbf{R}_j-\mathbf{R}_i$. Introducing a new integration variable

$$\boldsymbol{\varrho}\equiv\mathbf{r}-\tfrac{1}{2}(\mathbf{R}_i+\mathbf{R}_j)$$

and expanding the $\boldsymbol{\varrho}$-dependent part of exponential factor to terms linear in H, one has

$$S_{ji}=e^{ie(\mathbf{H}\times\mathbf{R}_{ji})\cdot(\mathbf{R}_i+\mathbf{R}_j)/4\hbar c}\int u(\boldsymbol{\varrho}+\tfrac{1}{2}\mathbf{R}_{ji})\times u(\boldsymbol{\varrho}-\tfrac{1}{2}\mathbf{R}_{ji})(1+ie\mathbf{H}\times\mathbf{R}_{ji}\cdot\boldsymbol{\varrho}/2\hbar c)d^3\rho.$$

Noting that the term in the integrand which is linear in

H is an odd[25] function of ϱ, and hence yields a vanishing contribution to the integral, one has

$$S_{ji}=S_{ji}^{(0)}e^{i\alpha_{ji}}, \tag{A14}$$

where

$$S_{ji}^{(0)}\equiv\int u(\varrho-\tfrac{1}{2}\mathbf{R}_{ji})u(\varrho+\tfrac{1}{2}\mathbf{R}_{ji})d^3\rho, \tag{A15}$$

and

$$\alpha_{ji}=-e\mathbf{H}\cdot\mathbf{A}_{ji}/\hbar c \tag{A16}$$

with

$$\mathbf{A}_{ji}\equiv\mathbf{R}_i\times\tfrac{1}{2}\mathbf{R}_j \tag{A17}$$

is clearly the area of the triangle whose vertices are the points $\mathbf{R}_i$, $\mathbf{R}_j$ and the origin.

It is to be noted that the phases α_{ji} are not unique—depending, in particular, on the arbitrary location of the origin, and, more generally, on the gauge of the vector potential. However, as shown in FH, the cyclic sum of the phases connecting any three sites is gauge invariant, viz.:

$$\alpha_{ji}+\alpha_{kj}+\alpha_{ik}=-(e/\hbar c)\mathbf{H}\cdot\mathbf{A}_{kji}, \tag{A18}$$

where

$$\mathbf{A}_{kji}=\mathbf{A}_{ji}+\mathbf{A}_{kj}+\mathbf{A}_{ik}=\mathbf{R}_{ji}\times\tfrac{1}{2}\mathbf{R}_{ki} \tag{A19}$$

is the area of the triangle whose vertices are the points $\mathbf{R}_i$, $\mathbf{R}_j$, and $\mathbf{R}_k$.

Turning now to the first term of (2.13), namely,

$$\mathcal{J}_{ji}\equiv-\int\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})[\sum_{k\neq i}U_k(\mathbf{r}-\mathbf{R}_k)]d^3r \tag{A20}$$

and rewriting it in the form

$$\mathcal{J}_{ji}=-\int\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})[V(\mathbf{r})-U_i(\mathbf{r}-\mathbf{R}_i)]d^3r, \tag{A20'}$$

where

$$V(\mathbf{r})\equiv\sum_k U(\mathbf{r}-\mathbf{R}_k) \tag{A21}$$

is the total (periodic) single-particle potential (possessing the symmetry of the rigid lattice), one obtains, upon using (2.8),

$$\mathcal{J}_{ji}=e^{i\alpha_{ji}}\left[\mathcal{J}_{ji}^{(0)}+\frac{ie\mathbf{H}\times\mathbf{R}_{ji}}{2\hbar c}\cdot\mathbf{K}_{ji}\right], \tag{A22}$$

where $\mathcal{J}_{ji}^{(0)}$ is the zero-field value of $\mathcal{J}_{ji}$, and where

$$\mathbf{K}_{ji}\equiv-\int u(\mathbf{r}-\mathbf{R}_i)u(\mathbf{r}-\mathbf{R}_j)[\mathbf{r}-(\mathbf{R}_i+\mathbf{R}_j)/2]\times[V(\mathbf{r})-U(\mathbf{r}-\mathbf{R}_i)]d^3r. \tag{A23}$$

It will now be shown that the term in (A22) proportional to $\mathbf{K}_{ji}$ vanishes provided that the crystal possesses some n-fold rotational symmetry about the axis $\mathbf{R}_{ji}$, joining sites i and j. In this case $U(\mathbf{r}-\mathbf{R}_i)$ [and hence the nondegenerate local eigenfunctions $u(\mathbf{r}-\mathbf{R}_i)$], as well as $V(\mathbf{r})$, possess this symmetry, so that the factor $u(\mathbf{r}-\mathbf{R}_i)u(\mathbf{r}-\mathbf{R}_j)[V(\mathbf{r})-U(\mathbf{r}-\mathbf{R}_i)]$ in the integrand of (A23) is invariant with respect to rotations, $2\pi p/n$ $\times(1\leq p<n)$ about the axis $\mathbf{R}_{ji}$. With this symmetry, it is then apparent that $\mathbf{K}_{ji}$ cannot have a component perpendicular to $\mathbf{R}_{ji}$, and that, hence, the scalar product $\mathbf{H}\times\mathbf{R}_{ji}\cdot\mathbf{K}_{ji}$ is zero, Q.E.D. Thus

$$\mathcal{J}_{ji}=e^{i\alpha_{ji}}\mathcal{J}_{ji}^{(0)} \tag{A24}$$

for all intersite axes possessing some n-fold ($n>1$) symmetry.

It may be remarked that, in the case that i and j are nearest neighbors (this being essentially the exclusive case of interest for the present paper), the required rotational symmetry is fulfilled for a wide variety of crystals. In particular, the nearest-neighbor axes for the two-dimensional hexagonal lattice, considered in FH, as well as the three-dimensional face-centered cubic lattice[26] possess at least twofold symmetry.

Introducing (2.24) and (2.14) into (2.13), one then has

$$J_{ji}^{(H)}=e^{i\alpha_{ji}}J_{ji}, \tag{A25}$$

where J_{ji} is the zero-field value of $J_{ji}^{(H)}$ [obtained by the replacement $\phi_i(\mathbf{r})\rightarrow u(\mathbf{r}-\mathbf{R}_i)$ in the integrals contained in (2.10) and (2.13)[27]].

The preceding discussion has concerned itself exclusively with the form of the "projected" electron (hole) Hamiltonian, as given by (2.11) [or (2.11')] and (2.25). The form of the other two components (the lattice term H_L and the interaction H_{int}) will now be considered.

The lattice Hamiltonian

$$\langle j|H_L|i\rangle=\sum_\lambda\hbar\omega_\lambda(b_\lambda^*b_\lambda+\tfrac{1}{2}) \tag{A26}$$

is taken to be a sum of contributions of harmonic-oscillator terms, each associated with a given lattice-vibration mode (indexed by the letter λ), with ω_λ the frequency and $b_\lambda^*(b_\lambda)$ the usual boson creation (destruction) operators—all pertaining to the λth mode.

The interaction term H_{int} arises from the dependence of the total one-electron potential on the lattice displacements, and, hence, on the b_λ, b_λ^*. Restricting the discussion to terms linear in the lattice displacements, one has for the most general perturbation of the one-

[25] This is so by virtue of the above introduced assumption that $u(\mathbf{r})$ is spherically or cylindrically symmetric about the field direction.

[26] These lattices have the property such that, for any two nearest-neighbor sites, there exists a (not necessarily unique) third site which is a nearest neighbor to the first two, i.e., the axes $\mathbf{R}_{ji}$, $\mathbf{R}_{kj}$, and $\mathbf{R}_{ik}$ are all nearest-neighbor axes. As shown in FH, such lattices provide the lowest-order Hall effect ($\sigma_{xy}\sim J^3$).

[27] It may finally be remarked that, as in Ref. 9, it is not essential for the argument of this paper that the quantity $\mathbf{A}_{kji}$, occurring in the basic "flux" relationship (A18) be equal precisely to the area of the triangle defined by the site centers $\mathbf{R}_i$, $\mathbf{R}_j$, and $\mathbf{R}_k$; order-of-magnitude correspondence is sufficient.

electron potential due to lattice displacements

$$V_{\rm int}(\mathbf{r})=(2N)^{-1/2}\sum_{\lambda}[V_\lambda(\mathbf{r})b_\lambda+V_\lambda^*(\mathbf{r})b_\lambda^*] \quad \text{(A27)}$$

[where N is the number of unit cells in the sample; the factor $(2N)^{-1/2}$ is introduced to give the correct volume dependence].

In this paper, it will be assumed that an adequate expression for $H_{\rm int}$ may be obtained by projecting $V_{\rm int}(\mathbf{r})$ onto the subspace spanned by the $\Phi_i(\mathbf{r})$ and retaining *only* the components diagonal in the site indices. If this recipe is followed, one has

$$\langle j|H_{\rm int}|i\rangle=\delta_{ij}\langle i|V_{\rm int}(\mathbf{r})|j\rangle=\delta_{ij}(2N)^{-1/2}\times\sum_{\lambda}[V_{\lambda i}e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i}b_\lambda+V_{\lambda i}^*e^{-i\mathbf{q}_\lambda\cdot\mathbf{R}_i}b_\lambda^*], \quad \text{(A28)}$$

where

$$V_{\lambda i}\equiv e^{-i\mathbf{q}_\lambda\cdot\mathbf{R}_i}\int V_\lambda(\mathbf{r})|\phi_i(\mathbf{r})|^2d^3r \quad \text{(A29)}$$

and where $\mathbf{q}_\lambda$ is the wave vector of the λth mode (assumed to be a "running" mode).

In the case of a periodic arrangement of electron (hole) occupation sites i it is readily shown that $V_{\lambda i}$ is independent of the site index i, i.e.,[28]

$$\langle j|H_{\rm int}|i\rangle=\delta_{ij}(2N)^{-1/2}\sum_{\lambda}[V_\lambda e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i}b_\lambda+V_\lambda^*e^{-i\mathbf{q}_\lambda\cdot\mathbf{R}_i}b_\lambda^*]. \quad \text{(A30)}$$

For the sake of simplicity, (A30) will henceforth be used, in place of the more general expression (A28).

At this point it is desirable to note the existence of an additional symmetry, namely, time-reversal invariance of $H_{\rm int}$ in the absence of a magnetic field.[29] With the lattice vibrations being described in terms of running modes, the time-reversal operation consists of (a) replacing the coefficients of the b_λ and b_λ^* in (A30) by their complex conjugates, and (b) replacing each field operator, $b_\lambda(b_\lambda^*)$ by $b_{-\lambda}(b_{-\lambda}^*)$, the notation "$-\lambda$" denoting the "time-reversed" mode of λ—i.e., the mode having the same polarization and frequency, but oppositely directed wave-vector ($\mathbf{q}_{-\lambda}=-\mathbf{q}_\lambda$). Carrying out this operation, one then notes that the required invariance of $H_{\rm int}$ leads to the relations

$$V_{-\lambda}=V_\lambda^*. \quad \text{(A31)}$$

Introducing (A31) into (A30), one then has

$$\langle j|H_{\rm int}|i\rangle=\delta_{ij}(2N)^{-1/2}\sum_{\lambda}e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i}[b_\lambda+b_{-\lambda}^*]V_\lambda. \quad \text{(A32)}$$

[28] The essence of the proof consists in noting that the square bracket in (2.28) must be invariant with respect to the displacement operation $\mathbf{R}_i\rightarrow\mathbf{R}_j$; $b_\lambda\rightarrow b_\lambda e^{-i\mathbf{q}_\lambda\cdot\mathbf{R}_{ji}}$.

[29] Under the restrictions already incorporated into the treatment, in which the sole effect of the magnetic field appears in the local-site wave functions [as given by (A8)], it is clear that $H_{\rm int}$ is independent of the magnetic field. Hence, the discussion actually applies for nonvanishing field, as well.

One now notes that, since the phases of the basic lattice-vibration wave functions are arbitrary, they can be chosen so as to multiply both b_λ and $b_{-\lambda}^*$ by an arbitrary phase factor $e^{i\delta_\lambda}$. (The adjoints of these operators, b_λ^* and $b_{-\lambda}$, of course, are multiplied by the adjoint phase factor $e^{-i\delta_\lambda}$.) Choosing the phase factors so that the quantities $V_\lambda e^{i\delta_\lambda}$ are real, one may thereby, without loss of generality, take the V_λ in (A32) to be real.

One may at this point introduce the canonical transformation of Refs. 3 and 4. However, in order to effect a correspondence with the earlier treatment of the present authors (FH), the alternate procedure of transforming to the Pekar-Buimistrov standing-wave modes will be followed. This is done via the canonical transformation

$$b_\lambda=(2)^{-1/2}[e^{-i\pi/4}B_\lambda+e^{i\pi/4}B_{-\lambda}], \quad \text{(A33a)}$$

$$b_{-\lambda}=(2)^{-1/2}[e^{-i\pi/4}B_{-\lambda}+e^{i\pi/4}B_\lambda] \quad \text{(A33b)}$$

to new Bose operators B_λ. Introducing (A33) into (A32), and utilizing (A31), one obtains

$$\begin{aligned}\langle j|H_{\rm int}|i\rangle&=\delta_{ij}(N)^{-1/2}\sum_{\lambda}V_\lambda\times\cos(\mathbf{q}_\lambda\cdot\mathbf{R}_i-\tfrac{1}{4}\pi)(B_\lambda+B_\lambda^*)\\&=\delta_{ij}N^{-1/2}\sum_{\lambda}V_\lambda\times\sin(\mathbf{q}_\lambda\cdot\mathbf{R}_i+\tfrac{1}{4}\pi)(B_\lambda+B_\lambda^*)\\&=\delta_{ij}(2/N)^{1/2}\sum_{\lambda}V_\lambda\sin(\mathbf{q}_\lambda\cdot\mathbf{R}_i+\tfrac{1}{4}\pi)Q_\lambda, \quad \text{(A34)}\end{aligned}$$

where the

$$Q_\lambda\equiv\tfrac{1}{2}(B_\lambda+B_\lambda^*)^{1/2} \quad \text{(A35)}$$

are Hermitian operators, playing the role of lattice-vibration coordinates, with

$$P_\lambda\equiv\tfrac{1}{2}(B_\lambda-B_\lambda^*)^{1/2}i=(1/i)(\partial/\partial Q_\lambda) \quad \text{(A36)}$$

the corresponding canonically conjugate Hermitian operators.

Reverting to the lattice Hamiltonian H_L one easily verifies that

$$\begin{aligned}\langle j|H_L|i\rangle&=\delta_{ji}\sum_{\lambda}\hbar\omega_\lambda(B_\lambda^*B_\lambda+\tfrac{1}{2}),\\&=\delta_{ji}\sum_{\lambda}\tfrac{1}{2}\hbar\omega_\lambda\left(Q_\lambda^2-\frac{\partial^2}{\partial Q_\lambda^2}\right). \quad \text{(A37)}\end{aligned}$$

From (A11′), (A25), (A34), and (A37), one then has for the total Hamiltonian

$$\langle j|H|i\rangle=-J_{ji}e^{i\alpha_{ji}}(1-\delta_{ji})+\delta_{ji}\sum_{\lambda}\left[\tfrac{1}{2}\hbar\omega_\lambda\left(Q_\lambda^2-\frac{\partial^2}{\partial Q_\lambda^2}\right)+(2/N)^{1/2}V_\lambda\sin(\mathbf{q}_\lambda\cdot\mathbf{R}_i+\tfrac{1}{4}\pi)Q_\lambda\right]. \quad \text{(A38)}$$

Comparing (A38) with the Hamiltonian of FH, as given by Eq. (3.2) of that work, one notes that, with the identifications

$$Q_\lambda \leftrightarrow (M\omega_k/\hbar)^{1/2} q_k , \tag{A39a}$$

$$V_\lambda \leftrightarrow -A(\hbar/M\omega_k)^{1/2}, \tag{A39b}$$

the correspondence between the two is complete. It then follows that, just as in FH, the eigenfunctions of that part of (A38) which is diagonal (in the site index) are

$$|i,\cdots N_\lambda^{(i)}\cdots\rangle = \Phi_i(\mathbf{r})\pi_\lambda \chi_{N_\lambda{}^{(i)}}(Q_\lambda - Q_\lambda^{(i)}), \tag{A40}$$

where the $\chi_N(Q)$ are normalized harmonic-oscillator functions, centered about "local-equilibrium" values

$$Q_\lambda{}^{(i)} = (2/N)^{1/2}(V_\lambda/\hbar\omega_\lambda)^{1/2} \sin(\mathbf{q}_\lambda\cdot\mathbf{R}_i + \tfrac{1}{4}\pi), \tag{A41}$$

and the corresponding eigenvalues are

$$\epsilon_{\cdots N_\lambda{}^{(i)}\cdots} = \sum_\lambda \hbar\omega_\lambda(N_\lambda{}^{(i)} + \tfrac{1}{2}) + E_b , \tag{A42}$$

where

$$E_b = (2/N)\sum_\lambda (V_\lambda{}^2/2\hbar\omega_\lambda)^{1/2} \sin^2(\mathbf{q}_\lambda\cdot\mathbf{R}_i + \tfrac{1}{4}\pi). \tag{A43}$$

In the representation of the states $|i,\cdots N_\lambda\cdots\rangle$, given by (A40), the remaining (nondiagonal) part of the Hamiltonian [i.e., the first term on the rhs of (A38)] becomes [cf. FH's Eq. (3.8)]

$$\begin{aligned}\langle j,\cdots N_\lambda{}^{(j)}\cdots|H|i,\cdots N_\lambda{}^{(i)}\cdots\rangle &\equiv \langle\cdots N_\lambda{}^{(j)}\cdots|V_{ji}{}^{(H)}|\cdots N_\lambda{}^{(i)}\rangle \\ = J_{ji}e^{\alpha ji}\times\pi_\lambda\Big\{1-\frac{4}{N}(N_\lambda{}^{(i)}+\tfrac{1}{2})\gamma_{ji,\lambda}\cos^2[\mathbf{q}_\lambda\tfrac{1}{2}(\mathbf{R}_i+\mathbf{R}_j)+\tfrac{1}{4}\pi]\Big\} \\ \times\delta_{N_\lambda{}^{(j)},N_\lambda{}^{(i)}}\mp\Big\{\Big(\frac{8}{N}\Big)^{1/2}\epsilon_{ji}\gamma_{ji,\lambda}{}^{1/2}\cos[\mathbf{q}_\lambda\cdot\tfrac{1}{2}(\mathbf{R}_i+\mathbf{R}_j)+\tfrac{1}{4}\pi]\tfrac{1}{2}(N_\lambda{}^{(i)}+\tfrac{1}{2}\pm\tfrac{1}{2})^{1/2}\Big\}\delta_{N_\lambda{}^{(j)},N_\lambda\pm1{}^{(i)}},\end{aligned} \tag{A44}$$

where

$$\gamma_{ji,\lambda} \equiv \tfrac{1}{2}[V_\lambda{}^2(\hbar\omega_\lambda)^2][1-\cos\mathbf{q}_\lambda\cdot\mathbf{R}_{ji}] \tag{A45}$$

and ϵ_{ji} is equal to ±1, according to whether[30] $\mathbf{q}_\lambda\cdot\mathbf{R}_{ji} \gtrless 0$.

APPENDIX B

In this Appendix, the equivalence of (3.2) and (3.3) to the standard Kubo formula for the dc conductivity tensor[31]

$$\sigma_{xy} = \frac{e^2}{ZV}\int_{-\infty}^{0} dt \int_0^\beta d\lambda\, e^{st}\,\mathrm{Tr}\{e^{-\beta H}e^{iH(t/\hbar - i\lambda)}v_y \times e^{-iH(t/\hbar - i\lambda)}v_x\} \tag{B1}$$

will be established. A straightforward proof may be achieved by expressing both (B1) and (3.2)–(3.3) in the representation of the eigenstates of H, i.e., those eigenstates ψ_n (and eigenvalues, E_n) of the equation

$$H\psi_n = E_n\psi_n .$$

Introducing this representation into (B1) and carrying out the integrations, one has

$$\sigma_{xy} = \frac{e^2\hbar}{iZV}\sum_{nm}\frac{e^{-\beta E_m}-e^{-\beta E_n}}{E_n-E_m}\frac{\langle n|v_y|m\rangle\langle m|v_x|n\rangle}{E_n-E_m-i\hbar s}. \tag{B2}$$

Proceeding similarly with (3.3), and replacing[32] $\hbar\omega_r$ by Ω, one has

$$\begin{aligned}\mathfrak{F}_{xy}(\Omega) &= \frac{1}{Z}\sum_{nm}\frac{e^{-\beta E_m}-e^{-\beta E_n}}{E_n-E_m+\Omega}\langle n|v_x|m\rangle\langle m|v_y|n\rangle , \\ &= \frac{1}{Z}\sum_{nm}\frac{e^{-\beta E_m}-e^{-\beta E_n}}{E_n-E_m-\Omega}\langle n|v_y|m\rangle\langle m|v_x|n\rangle ,\end{aligned} \tag{B3}$$

the last equality arising from an interchange of the summation indices, n and m. Inserting this last equality into (3.2), one has

$$\begin{aligned}\sigma_{xy} &= \frac{e^2\hbar}{i\Omega ZV}\sum_{nm}(e^{-\beta E_m}-e^{-\beta E_n})\langle n|v_y|m\rangle\langle m|v_x|n\rangle \\ &\quad\times\Big[\frac{1}{E_n-E_m-\Omega}-\frac{1}{E_n-E_m}\Big] \\ &= \frac{e^2\hbar}{iZV}\sum_{nm}\frac{e^{-\beta E_m}-e^{-\beta E_n}}{(E_n-E_m)(E_n-E_m-\Omega)} \\ &\quad\times\langle n|v_y|m\rangle\langle m|v_x|n\rangle .\end{aligned} \tag{B4}$$

Bearing in mind the definition of Ω, namely $\Omega = h(\omega + is)$, one sees that, in the limit $\omega = 0$, (B4) coincides with (B2).[33]

[30] The notation $\langle\cdots N_\lambda{}^{(j)}\cdots|V_{ji}{}^{(H)}|\cdots N_\lambda{}^{(i)}\cdots\rangle$ is introduced to establish the connection with the text notation of Eq. (2.1) *et seq.* Here, the superscript "(H)" denotes magnetic field dependence.

[31] Refer to, e.g., Eq. (3.1) of Ref. 4.

[32] Before carrying out this replacement, one must utilize (3.4) to substitute unity in place of the factor $e^{\hbar\omega_r\beta}$ wherever that factor occurs in the integrated expression for $\mathfrak{F}_{xy}(\hbar\omega_r)$; otherwise, $\mathfrak{F}_{xy}(\Omega)$ will not be analytic in each half of the complex plane.

[33] The proof could easily have been generalized to establish the (more general) equivalence of (3.2)–(3.3) to the expression for $\sigma_{xy}(\omega)$ given in Kubo's original paper [J. Phys. Soc. Japan **12**, 570 (1957), Eq. (5.11)].