Hall Effect in Impurity Conduction*

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The existence of a nonvanishing Hall effect in the "impurity conduction" regime of a semiconductor is demonstrated. In this regime (prevalent at low temperatures and at low impurity concentrations) the dominant electron transport mechanism is the phonon-induced hopping of charge carriers from occupied to unoccupied majority sites. The basic element of the theory is the existence of a (magnetic) field-dependent contribution to the jump probability between two sites. This contribution is computed and is shown to arise from the interference between the amplitude for a direct transition between the initial and final sites and the amplitude for an indirect, second-order transition, involving intermediate occupancy of a third site.

The theory is applied to the case of an ac applied electric field. For values of the physical parameters representative of those occurring, for example in the ac measurements of Pollak and Geballe, the maximum Hall angle, though small ($\sim 10^{-6}$), is found to exceed the "normal" value $[(H/c)\mu_{\text{drift}}]$ by a factor $\sim 10^2$.

INTRODUCTION

THE existence of a Hall-effect in hopping-type electronic transport has been a question of interest for a number of years. In some recent studies of Friedman and the present author[1] on a particular hopping process—that of thermally activated small-polaron[2] motion—it has been established that a Hall effect comparable to, or even larger than the "normal" effect (Hall constant $R=-1/nec$) should exist. The present paper constitutes an extension of the ideas developed in the above-cited small-polaron studies to the investigation of the Hall effect in another hopping-type transport process, namely *impurity conduction*.[3]

The physical picture of impurity conduction may be described briefly as follows. Let it be assumed, for the sake of definiteness, that the sample is n type, with donor and acceptor concentrations N_D and N_A ($N_D > N_A$). At sufficiently low temperatures, such that the number of electrons in the conduction band is negligible, the acceptors and an equal number of donors will be ionized, negatively and positively, respectively; a fraction $(N_D-N_A)/N_D$ of the donor sites will be occupied by electrons. Charge transport will then occur by virtue of the hopping of these electrons from filled to unfilled donor levels.

An integral feature of the hopping process is its dependence on electron-lattice interaction. This dependence arises from the circumstance that, because of the random nature of the Coulombic potentials of the ionized constituents (donors and acceptors), the energies of any two local donor states are not coincident. It then follows that, in order for a hopping transition to occur, energy must be exchanged with some "reservoir." Such an exchange is provided by interaction with the lattice vibrations. A consequence of this interaction is that hopping is always accompanied by the emission or absorption of one or more phonons.

In the case of ordinary (nonmagnetic) transport phenomena, the basic elementary process is the above-described hopping transition between two sites. Now, from symmetry considerations alone, the effect of a magnetic field on such two-site processes cannot give rise to a nonvanishing Hall effect. A minimum of three sites is necessary; as will be shown below, it is also sufficient. In particular, it will be demonstrated that the relative probabilities of an electron, initially located on one of three sites, hopping to one or the other of the remaining two sites (assumed to be initially unoccupied) is modified by a contribution which, both in sign and magnitude, is linearly proportional to the applied magnetic field. As in the case of the small polaron,[1] the effect will be seen to arise from the interference between the amplitude for a *direct* transition between the initial and final sites, and the amplitude for an indirect, second-order transition, involving intermediate occupancy of the third site.

The treatment of the effect of the magnetic field on three-site transition processes is given in Sec. I. Results comparable in generality to, e.g., the expressions given by Miller and Abrahams for the ordinary two-site transitions [cf. Eq. (II-14) of reference 3] are obtained. However, just as in the treatment of the cited authors,[3] in order to arrive at bulk transport properties, such as electrical conductivity (or, as in the present work, Hall mobility) it is necessary to consider sequences of two-site and three-site jumps, in which (by virtue of the random distribution of impurity centers) the elementary jump probabilities undergo large fluctuations. The solution of the resultant statistical problem is beset with formidable difficulties. In the present paper, these difficulties are largely avoided by restricting the treatment to the case of an applied ac electric field. Here, as shown by Pollak and Geballe,[4] when the applied frequency is sufficiently high, the dominant contributions to, e.g., electrical conductivity, arise from

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[1] L. Friedman, thesis (unpublished); L. Friedman and T. Holstein, Bull. Am. Phys. Soc. 6, 302 (1961); and to be published. The present treatment does not require reference to the small-polaron studies.

[2] T. Holstein, Ann. Phys. 8, 325, 343 (1959).

[3] An extensive theoretical treatment of impurity conduction is given in the recent paper of A. Miller and E. Abrahams, Phys. Rev. 120, 745 (1960), to which further reference will be made.

[4] M. Pollak and T. H. Geballe, Phys. Rev. 122, 1742 (1961).

single hopping acts between individual pairs (with sequences of jumps among larger aggregates of sites playing a negligible role). In Sec. II of the present paper, an analysis comparable to that of Pollak and Geballe is given for three-site transitions in the presence of an ac electric field and a dc magnetic field. Semiquantitatively accurate expressions are obtained for ac Hall conductivity and Hall mobility. As in the case of the small polaron,[1] it turns out that, at least under conditions prevailing in the experiments of Pollak and Geballe, these quantities, though small, exceed their "normal" values by a factor in excess of 10^2.

In the last section, a brief discussion of the sign of the Hall coefficient is given. It is concluded that the sign is negative.

I. THREE-SITE TRANSITION PROBABILITIES

Ignoring the effects of the magnetic field for the time being, one has for the Hamiltonian of a (one-electron) three-site system

$$H=H_e+H_{\rm int}+H_L. \tag{1.1}$$

Here H_e is that part of the Hamiltonian which depends only on the electronic coordinate; it takes the form[5]

$$H_e=T+V_a(r) - (e^2/\kappa)\left[\frac{1}{|\mathbf{r}-\mathbf{R}_1|}+\frac{1}{|\mathbf{r}-\mathbf{R}_2|}+\frac{1}{|\mathbf{r}-\mathbf{R}_3|}\right], \tag{1.2}$$

where T is the effective-mass kinetic-energy operator, $-e^2/\kappa|\mathbf{r}-\mathbf{R}_i|$ is the potential energy of the electron in the field of the ith donor site (the center of which is located at E_i), and V_a is the potential due to other ionized constituents.[6] In the present work, the multivalley features incorporated in the treatment of Miller and Abrahams[3] will be ignored; the kinetic energy operator will thus be taken to have the form

$$T=-(\hbar^2/2m^*)\nabla^2. \tag{1.3}$$

The second member of (1.1) is the electron-lattice interaction; in the case of the simplified model represented by (1.3), it is given by the standard deformation-potential expression

$$H_{\rm int}=E_1\eta(\mathbf{r}), \tag{1.4}$$

where E_1 is the deformation-potential constant, and where

$$\eta(\mathbf{r})=i\sum_\lambda \mathbf{q}_\lambda\cdot\mathbf{e}_\lambda\left(\frac{1}{N}\right)^{\frac{1}{2}}\left(\frac{\hbar}{2M\omega_\lambda}\right)^{\frac{1}{2}} \times(b_\lambda e^{i\mathbf{q}_\lambda\cdot\mathbf{r}}-b_\lambda^* e^{-i\mathbf{q}_\lambda\cdot\mathbf{r}}) \tag{1.5}$$

is the lattice-dilatation, expressed in terms of the polarization vectors, $\mathbf{e}_\lambda$, frequencies ω_λ, wave vectors $\mathbf{q}_\lambda$, and creation-annihilation operators b_λ^*, b_λ of the individual lattice-vibration modes (indexed by the subscript λ); the remaining undefined symbols in (1.5) are the atomic mass M and number N of atoms in the host crystal. It will eventually be assumed that the crystal is elastically isotropic; in that case only longitudinal modes will contribute to (1.4).

Finally, the lattice-vibration Hamiltonian H_L is given by the expression

$$H_L=\textstyle\sum_\lambda \hbar\omega_\lambda(b_\lambda^* b_\lambda+\frac{1}{2}). \tag{1.6}$$

Turning first to the discussion of the eigenstates of H_e, one notes that, in the event of sufficiently large inter-site separation, they take the form of isolated donor wave functions,[7]

$$\phi_i(\mathbf{r})\equiv\phi(\mathbf{r}-\mathbf{R}_i), \quad (i=1,2,3). \tag{1.7}$$

At separations which, though finite, are still large compared to the spatial extension of the ϕ_i's, the (three lowest) eigenfunctions of H_e may be approximated by linear combinations of the ϕ_i's, viz.

$$\psi_\alpha=\textstyle\sum_i C_i^{(\alpha)}\phi_i(\mathbf{r}); \quad \alpha=1,2,3.$$

Explicit expressions for the ψ_α are obtained in Appendix I by the standard atomic-orbital approach. The results are [cf. Eqs. (I16) of Appendix I]

$$\psi_1=\phi_1+[J_{21}/(\epsilon_1-\epsilon_2)]\phi_2+[J_{31}/(\epsilon_1-\epsilon_3)]\phi_3, \tag{1.8a}$$

$$\psi_2=[J_{12}/(\epsilon_2-\epsilon_1)]+\phi_2+[J_{32}/(\epsilon_2-\epsilon_3)]\phi_3, \tag{1.8b}$$

$$\psi_3=[J_{13}/\epsilon_3-\epsilon_1)]\phi_1+[J_{23}/(\epsilon_3-\epsilon_2)]\phi_2+\phi_3, \tag{1.8c}$$

where [cf. Eqs. (I12), (I18), (I19), and (I20) of

[5] cf. reference 3, p. 747; the expression given here is a straightforward generalization of the two-site Hamiltonian used by these authors.

[6] Strictly speaking, the case being considered here is appropriate to the regime of almost complete compensation. In order to treat the more interesting regime of small compensation, some modification of (1.2) will be required to take account of the circumstance that, in this latter domain, the most of the donor sites are occupied, so that conduction occurs via the motion of "holes" (rather than electrons). A proper treatment of this case would require taking explicit account of the many-electron nature of the problem. From this standpoint, the present one-electron treatment is to be regarded as preliminary; it is however anticipated that, within the domain of an over-all Heitler-London description of the electronic state of the system, the generalization to the actual many-electron case will be straightforward. In anticipation, it may here be remarked that in the case of small compensation, as pointed out by Miller and Abrahams, $V_a(\mathbf{r})$ is to be considered as arising from the nearest acceptor.

[7] In the present work, $\phi(\mathbf{r}-\mathbf{R}_i)$ will be assumed to refer to the ground-state donor wave function; complications due to energetic proximity of exicted states (occurring in some cases) will be ignored.

Appendix I]

$$\epsilon_i = E_d - \sum_{k\neq i} e^2/\kappa\,|\mathbf{R}_i-\mathbf{R}_k| + V_a(\mathbf{R}_i), \tag{1.9}$$

$$S_{ji} = \int \phi_j^* \phi_i dV, \tag{1.10}$$

$$J_{ji} = \int \phi_j^* \phi_i w_{ji}(\mathbf{r}) dV - (\epsilon_i-\epsilon_j)S_{ji}/2, \tag{1.11}$$

$$w_{ji}(\mathbf{r}) = -(e^2/\kappa)\left(\frac{1}{|\mathbf{r}-\mathbf{R}_j|}-\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|}\right) - (e^2/\kappa)\left(\frac{1}{|\mathbf{r}-\mathbf{R}_k|}-\frac{1}{2\,|\mathbf{R}_i-\mathbf{R}_k|}-\frac{1}{2\,|\mathbf{R}_j-\mathbf{R}_k|}\right) + \{V_a(\mathbf{r})-\tfrac{1}{2}[V_a(\mathbf{R}_i)+V_a(\mathbf{R}_j)]\}, \tag{1.12}$$

with the index k now denoting the third site ($k\neq i,j$).

The stage has now been reached where the effects due to a nonvanishing magnetic field may conveniently be considered. Neglecting the spin-Zeeman energy of the electron (this neglect being equivalent to the assumption that the spin-state of the electron remains unchanged in hopping transitions), one has for the electronic Hamiltonian

$$H_e = \frac{1}{2m^*}\left(\mathbf{p}+\frac{e\mathbf{A}}{c}\right)^2 + V_a(\mathbf{r}) - (e^2/\kappa) \times\left[\frac{1}{|\mathbf{r}-\mathbf{R}_1|}+\frac{1}{|\mathbf{r}-\mathbf{R}_2|}+\frac{1}{|\mathbf{r}-\mathbf{R}_3|}\right], \tag{1.13}$$

where the vector-potential, $\mathbf{A}$, is taken to have the form

$$\mathbf{A} = \tfrac{1}{2}\mathbf{H}\times\mathbf{r}, \tag{1.14}$$

$\mathbf{H}$ being the (spatially constant) magnetic field and $\mathbf{r}$ the electron coordinate, measured from an arbitrary origin. Following a procedure due to Zilberman[8] one redefines the basic local functions $\phi_i(\mathbf{r})$ to be solutions of the equations

$$\left[\frac{1}{2m^*}\left(\mathbf{p}+\frac{e\mathbf{A}}{c}\right)^2 - \frac{e^2}{\kappa\,|\mathbf{r}-\mathbf{R}_i|}\right]\phi_i(\epsilon) = E_d\phi_i(\mathbf{r}). \tag{1.15}$$

These solutions will obviously not be of the form $\phi(\mathbf{r}-\mathbf{R}_i)$; however, if one introduces the gauge transformation

$$\phi_i(\mathbf{r}) = u_i(\mathbf{r})e^{-i\chi_i(\mathbf{r})}, \tag{1.16}$$

with

$$\chi_i(\mathbf{r}) = e\mathbf{A}(\mathbf{R}_i)\cdot\mathbf{r}/\hbar c = (e/2\hbar c)(\mathbf{H}\times\mathbf{R}_i)\cdot\mathbf{r}, \tag{1.17}$$

one has, in place of (1.15)

$$\left[\frac{1}{2m^*}\left(\mathbf{p}+\frac{e}{2c}\mathbf{H}\times(\mathbf{r}-\mathbf{R}_i)\right)^2 - e^2/\kappa\,|\mathbf{r}-\mathbf{R}_i|\right]u_i(\mathbf{r}) = E_d u_i(\mathbf{r}), \tag{1.18}$$

the solution of which is clearly of the form

$$u_i(\mathbf{r}) = u(\mathbf{r}-\mathbf{R}_i). \tag{1.19}$$

Just as in the absence of the magnetic field, one now assumes that the eigenstates of the total electronic Hamiltonian (1.13) may be represented as a superposition of the three ϕ_i's. Then, upon following the atomic orbital "projection" routine of Appendix I, one reobtains equations (1.8a,b,c), together with (1.9), (1.10), (1.11), and (1.12), the effects of the magnetic field being contained entirely in the $\phi_i(\mathbf{r})$ [as given by (1.16)].

It should at this point be remarked that the basic local functions, $u(\mathbf{r}-\mathbf{R}_i)$, as well as the associated energy eigenvalue, E_d, depend upon the magnetic field. If, however, for the sake of simplicity, the zero-field functions be assumed to be non-degenerate s functions, first-order terms in H disappear from (1.18), and one is left with the H^2 diamagnetic corrections to $u(\mathbf{r}-\mathbf{R}_i)$ and E_d. These corrections are irrelevant for the theory of this paper, which is concerned only with effects linear in H. Hence, in what follows, they shall be ignored. This means in particular that the field-dependence of the ϕ_i's is contained entirely in the gauge factors, $e^{-i\chi_i(\mathbf{r})}$, defined by (1.17).

Thus, upon inserting (1.16) into (1.9), (1.10), and (1.11), and employing (1.17), one obtains[9]

$$\epsilon_i(H) = \epsilon_i, \tag{1.20}$$

$$J_{ji}(H) = \int u(\mathbf{r}-\mathbf{R}_j)u(\mathbf{r}-\mathbf{R}_i)w_{ji}(\mathbf{r}) \times\exp\{(ie/2\hbar c)[\mathbf{H}\times(\mathbf{R}_j-\mathbf{R}_i)]\cdot\mathbf{r}\}dV - \frac{(\epsilon_i-\epsilon_j)}{2}\int u(\mathbf{r}-\mathbf{R}_j)u(\mathbf{r}-\mathbf{R}_i) \times\exp\{(ie/2\hbar c)[\mathbf{H}\times(\mathbf{R}_j-\mathbf{R}_i)\cdot\mathbf{r}]\}dV, \tag{1.21}$$

where ϵ_i is, as before, the zero-field value of local site energy.

In proceeding further, one conveniently takes the origin of the coordinate system to be located within the

[8] G. E. Zilberman, Soviet Phys.—JETP **2**, 650 (1956); the procedure used in the present paper is actually slightly different from Zilberman's in that, as pointed out in the text contained between Eqs. (1.19) and (1.20), the first-order dependence of the local wave functions on the magnetic field is expressed entirely in the exponential factor of (1.16), whereas Zilberman's local functions contain an implicit (linear) field dependence. Neglect of this implicit dependence, while not serious for the problem treated by him, would yield incorrect (in fact, non-gauge-invariant) results for the case treated here. (cf. reference 1, Appendix E of Friedman's thesis).

[9] $u(\mathbf{r}-\mathbf{R}_i)$, being nondegenerate, may be taken to be real.

triangle defined by the geometric centers of the three sites. Then, subject to the assumption

$$(eH/2\hbar c)|\mathbf{R}_j-\mathbf{R}_i|^2\ll 1, \tag{1.22}$$

one may replace the gauge-exponentials by their Taylor expansions to terms linear in H. One then obtains, after some algebraic manipulation

$$J_{ji}(H)=W_{ji}e^{i\alpha_{ji}}-\frac{(\epsilon_i-\epsilon_j)}{2}S_{ji}e^{i\beta_{ji}}, \tag{1.23}$$

where

$$W_{ji}=\int u(\mathbf{r}-\mathbf{R}_j)u(\mathbf{r}-\mathbf{R}_i)w_{ji}(\mathbf{r})dV, \tag{1.24}$$

$$\alpha_{ji}=\frac{e}{2\hbar c}[\mathbf{H}\times(\mathbf{R}_j-\mathbf{R}_i)\cdot\boldsymbol{\varrho}_{ji}^{(1)}], \tag{1.25}$$

$$\boldsymbol{\varrho}_{ji}^{(1)}=W_{ji}^{-1}\int u(\mathbf{r}-\mathbf{R}_j)u(\mathbf{r}-\mathbf{R}_i)w_{ji}(\mathbf{r})\mathbf{r}dV, \tag{1.26}$$

$$S_{ji}=\int u(\mathbf{r}-\mathbf{R}_j)u(\mathbf{r}-\mathbf{R}_i)dV, \tag{1.27}$$

$$\beta_{ji}=\frac{e}{2\hbar c}[\mathbf{H}\times(\mathbf{R}_j-\mathbf{R}_i)\cdot\boldsymbol{\varrho}_{ji}^{(2)}], \tag{1.28}$$

$$\boldsymbol{\varrho}_{ji}^{(2)}=S_{ji}^{-1}\int u(\mathbf{r}-\mathbf{R}_i)u(\mathbf{r}-\mathbf{R}_j)\mathbf{r}dV. \tag{1.29}$$

It may here be observed that, by virtue of the s character of the u's, $\boldsymbol{\varrho}_{ji}^{(2)}$ coincides with the point $(\mathbf{R}_i+\mathbf{R}_j)/2$ midway between sites i and j. Inserting this equality into (1.28), one has

$$\beta_{ji}=(e/\hbar c)\mathbf{H}\cdot\mathbf{A}_{ji}, \tag{1.30}$$

where

$$\mathbf{A}_{ji}\equiv\mathbf{R}_j\times\mathbf{R}_i/2 \tag{1.31}$$

is the vector area of the triangle defined by sites i and j, and the origin of the coordinate system. From this result, it follows immediately that

$$\beta_{21}+\beta_{32}+\beta_{13}=(e/\hbar c)\mathbf{H}\cdot\mathbf{A}_{321}, \tag{1.32}$$

where $\mathbf{A}_{321}$ is the vector area of the triangle defined by the three sites under consideration.

Unfortunately, the quantities $\boldsymbol{\varrho}_{ji}^{(1)}$ and α_{ji} do not appear to be describable in comparably simple geometrical terms. Namely, because of the presence of $V_a(\mathbf{r})$ and $-e^2/\kappa|\mathbf{r}-\mathbf{R}_k|$ $(k\neq i, j)$ in the integrand of (1.26), the vector $\boldsymbol{\varrho}_{ji}^{(1)}$ will not, in general, terminate on the line joining sites i and j; hence, the effective "flux" area

$$\mathfrak{A}_{321}=\mathfrak{A}_{21}+\mathfrak{A}_{32}+\mathfrak{A}_{13}, \tag{1.33}$$

where

$$\mathfrak{A}_{ji}\equiv(\mathbf{R}_j-\mathbf{R}_i)\times\boldsymbol{\varrho}_{ji}^{(1)} \tag{1.34}$$

will not coincide exactly with the geometrical[10] area, $\mathbf{A}_{321}$.

The next stage in the treatment is the computation of the matrix elements of electron-phonon interaction,

$$(i|H_{\text{int}}|j)=\int\psi_j^*(\mathbf{r})\eta(\mathbf{r})\psi_i(\mathbf{r})dV. \tag{1.35}$$

The detailed computation of these matrix elements is given in Appendix II; the results are [cf. Eqs. (II4), (II7), and (II9)]

$$(j|H_{\text{int}}|i)=iE_1\sum_\lambda\mathbf{q}_\lambda\cdot\mathbf{e}_\lambda\left(\frac{\hbar}{2M\omega_\lambda}\right)^{\frac{1}{2}}\times(b_\lambda A_{ji}^{(\lambda)}-b_\lambda^\dagger A_{ji}^{(\lambda)\dagger}), \tag{1.36}$$

where

$$A_{ji}^{(\lambda)}=\delta_{ji}e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i}+(1-\delta_{ji})\left\{\frac{W_{ji}}{\epsilon_i-\epsilon_j}(e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_j}-e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i})e^{+i\alpha_{ji}}-\tfrac{1}{2}S_{ji}(e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_j}+e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i})e^{i\beta_{ji}}\right\}. \tag{1.37}$$

In proceeding further, it appears desirable, at least in this initial study, to effect some simplification of (1.37), which will nevertheless retain the essential physical effects. A possible simplification, already contained in the work of Miller and Abrahams,[3] consists in the neglect of the terms proportional to S_{ij}; its physical basis is the (presumed) relative smallness of local energy differences, $\epsilon_i-\epsilon_j$, as compared to the principal term, $-e^2/\kappa|\mathbf{r}-\mathbf{R}_j|$, in the "transfer potential," $W_{ji}(\mathbf{r})$ (which occurs in the integral for W_{ji}). In this connection the following observations are pertinent:

(a) As will be seen later in Sec. II, the three-site configurations which are of principal significance for the ac Hall effect are "equilateral" $(R_{ij}\cong R_{ik}\cong R_{ik})$. For such geometries the contributions to $\epsilon_i-\epsilon_j$ arising from the third site, k, [cf. (1.9)] essentially cancel.

(b) As will also be seen later in Sec. II, the inter-site distances of the important three-site configurations are somewhat less than the average distance between donors, and therefore rather less than the average distance between a donor and an acceptor atom. In this case, $V_a(\mathbf{R}_i)-V_a(\mathbf{R}_j)$ is also small.

Under these circumstances, it appears that the proposed simplification should not give rise to any gross errors; since the treatment of the present paper does not pretend to be more than semiquantitatively accurate, (1.37) will forthwith be replaced by

$$A_{ji}^{(\lambda)}=\delta_{ji}e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i}+(1-\delta_{ji})\frac{W_{ji}}{\epsilon_i-\epsilon_j}e^{i\alpha_{ji}}\times(e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_j}-e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i}).$$

[10] However, in view of the usual smallness of $V_a(\mathbf{r})$ and $e^2/\kappa|\mathbf{r}-\mathbf{R}_k|$ (relative to the principal two-center perturbation term, $-e^2/\kappa|\mathbf{r}-\mathbf{R}_i|$, in the integrand of (1.26), $\mathfrak{A}_{321}$ and $\mathbf{A}_{321}$ may, at least, be expected to have the same sign as well as the same order of magnitude.

The matrix elements of (1.36) between different lattice-vibration states may now be written down. They are

$$(j, N_\lambda \mp 1 \,|H_{\rm int}|\, i, N_\lambda) = E_1 D_\lambda^{(\pm)} \Big[\delta_{ji} e^{\pm i\mathbf{q}_\lambda \cdot \mathbf{R}_i} + (1-\delta_{ji}) \frac{W_{ji}}{\epsilon_i - \epsilon_j} e^{i\alpha_{ji}} (e^{\pm i\mathbf{q}_\lambda \cdot \mathbf{R}_j} - e^{\pm i\mathbf{q}_\lambda \cdot \mathbf{R}_i}) \Big], \quad (1.38)$$

where

$$D_\lambda^{(\pm)} \equiv \pm i(\mathbf{q}_\lambda \cdot \mathbf{e}_\lambda) \left(\frac{\hbar}{2MN\omega_\lambda} \right)^{\frac{1}{2}} (N_\lambda + \tfrac{1}{2} \mp \tfrac{1}{2})^{\frac{1}{2}}, \quad (1.39)$$

it being understood that all the N_λ's other than the given one under consideration remain fixed.

The stage has now been reached where the various higher order processes giving rise to the (magnetic) field-dependent part of the jump probabilities may be formulated. Broadly speaking, they are of two varieties:

(1) A superposition of two two-stage processes, one of which is $(i, N_\lambda, N_{\lambda'} \to j, N_\lambda \mp 1, N_{\lambda'} \to k, N_\lambda \mp 1, N_{\lambda'} \mp 1)$, the other being $(i, N_\lambda, N_{\lambda'} \to i, N_\lambda \mp 1, N_{\lambda'} \to k, N_\lambda \mp 1, N_{\lambda'} \mp 1)$.

(2) A superposition of a one-stage and a three-stage process; the first is of the form $(i, N_\lambda, N_{\lambda'} \to k, N_\lambda \mp 1, N_{\lambda'})$ whereas, a typical three-stage process is $(i, N_\lambda, N_{\lambda'} \to i, N_\lambda \mp 1, N_{\lambda'} \to j, N_\lambda \mp 1, N_{\lambda'} \mp 1 \to k, N_\lambda \mp 1, N_{\lambda'})$. These transitions, together with those which result from alterations of the sequences of various subprocess have all to be considered.

Let us begin with category (1), i.e., the two-stage processes, leading to changes in the population of two phonon modes, λ and λ'. Denoting the amplitude of the first subcategory, in which only the sites i and k are involved, by $(k, N_\lambda \mp 1, N_{\lambda'} \mp 1 \,|T_1|\, i, N_\lambda, N_{\lambda'})$, one has

$$\begin{aligned}(k, N_\lambda \mp 1, N_{\lambda'} \mp 1 \,|T_1|\, i, N_\lambda, N_{\lambda'}) &= \frac{(k, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, k, N_{\lambda'})(k, N_\lambda \mp 1 \,|H_{\rm int}|\, i, N_\lambda)}{\epsilon_i - \epsilon_k \pm \hbar\omega_\lambda} \\ &+ \frac{(k, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, i, N_{\lambda'})(i, N_\lambda \mp 1 \,|H_{\rm int}|\, i, N_\lambda)}{\pm \hbar\omega_\lambda} \\ &+ \frac{(k, N_\lambda \mp 1 \,|H_{\rm int}|\, k, N_\lambda)(k, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, i, N_{\lambda'})}{\epsilon_i - \epsilon_k \pm \hbar\omega_{\lambda'}} \\ &+ \frac{(k, N_\lambda \mp 1 \,|H_{\rm int}|\, i, N_\lambda)(i, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, i, N_{\lambda'})}{\pm \hbar\omega_{\lambda'}}. \end{aligned} \quad (1.40)$$

A degree of simplification can be effected by noting that, in any real transition, the energy-conservation condition

$$\epsilon_i - \epsilon_k \pm \hbar\omega_\lambda \pm \hbar\omega_{\lambda'} = 0 \quad (1.41)$$

must apply. Also, as will be seen later, the phonon energies are not arbitrary; one of them, say $\hbar\omega_\lambda$, will be shown to obey the "intermediate" energy-conservation relationship[11]

$$\epsilon_i - \epsilon_j \pm \hbar\omega_\lambda = 0, \quad (1.42)$$

so that

$$\epsilon_j - \epsilon_k \pm \hbar\omega_{\lambda'} = 0. \quad (1.43)$$

Introducing these conditions into (1.40), one has

$$\begin{aligned}(k, N_\lambda \mp 1, N_{\lambda'} \mp 1 \,|T_1|\, i, N_\lambda, N_{\lambda'}) &= \frac{(k, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, k, N_{\lambda'})(k, N_\lambda \mp 1 \,|H_{\rm int}|\, i, N_\lambda) - (k, N_\lambda \mp 0 \,|H_{\rm int}|\, i, N_\lambda)(i, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, i, N_{\lambda'})}{\epsilon_j - \epsilon_k} \\ &+ \frac{(k, N_\lambda \mp 1 \,|H_{\rm int}|\, k, N_\lambda)(k, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, i, N_\lambda) - (k, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, i, N_{\lambda'})(i, N_\lambda \mp 1 \,|H_{\rm int}|\, i, N_\lambda)}{\epsilon_i - \epsilon_j}. \end{aligned} \quad (1.44)$$

Instead of proceeding further with (1.44), it is at this point expedient to write down the other two-stage process, namely, that involving the jth side in the intermediate stage. In doing this, it will be convenient to employ the artifice of adiabatic "switching on" of the electron-lattice interaction, according to the time dependence, e^{st} (with eventual passage to the limit $s \to 0$). One then has

$$\begin{aligned}(k, N_\lambda \mp 1, N_{\lambda'} \mp 1 \,|T_2|\, i, N_\lambda, N_{\lambda'}) &= \frac{(k, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, j, N_{\lambda'})(j, N_\lambda \mp 1 \,|H_{\rm int}|\, i, N_\lambda)}{\epsilon_i - \epsilon_j \pm \hbar\omega_\lambda + i\hbar s} \\ &+ \frac{(k, N_\lambda \mp 1 \,|H_{\rm int}|\, j, N_\lambda)(j, N_{\lambda'} \mp 1 \,|H_{\rm int}|\, i, N_{\lambda'})}{\epsilon_i - \epsilon_j \pm \hbar\omega_{\lambda'} + i\hbar s}. \end{aligned} \quad (1.45)$$

It will now be noted from (1.42) and (1.43) that, in the first of the terms on the right-hand side of (1.45), intermediate energy is conserved, whereas in the second it is not (except in the very special case of $\epsilon_i - \epsilon_j = \epsilon_j - \epsilon_k$, the occurrence probability of which is negligibly small). As in the case of the small polaron, a field-dependent constructive interference between the two types of two-stage processes will be seen to result only when the zero-field amplitudes are 90° out of phase. Apart from the "phonon" phase-factors, $e^{i\mathbf{q}_\lambda \cdot \mathbf{R}_i}$ (the coherence features of which will be considered in detail, below) it can be seen from (1.38) and (1.39) that the zero-field amplitude of $(k, N_\lambda \mp 1, N_{\lambda'} \mp 1 \,|T_1|\, i, N_\lambda, N_{\lambda'})$ is necessarily real (again with the exception of the negli-

[11] That is, in the sense of time-dependent perturbation theory, in which $\epsilon_i - \epsilon_j \pm \hbar\omega_\lambda = ihs$ with $s \to 0$.

gibly probable cases $\epsilon_i=\epsilon_j$ or $\epsilon_j=\epsilon_k$); hence the zero-field amplitude of $(k, N_\lambda\mp1, N_{\lambda'}\mp1|T_2|i, N_\lambda, N_{\lambda'})$ will have to be imaginary. This requirement cannot be fulfilled unless, in the course of summing over λ or λ', a zero in one of the energy denominators is encountered. By virtue of (1.42) and (1.43), such an eventuality can occur only for the first term of (1.45); hence, it alone will be retained in what follows.[12] Thus

$$(k, N_\lambda\mp1, N_{\lambda'}\mp1|T_2^{(\mathrm{eff})}|i, N_\lambda, N_{\lambda'}) = \frac{(k, N_{\lambda'}\mp1|H_{\mathrm{int}}|j, N_{\lambda'})(j, N_\lambda\mp1|H_{\mathrm{int}}|i, N_\lambda)}{\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda+i\hbar s}, \tag{1.46}$$

which, with the use of (1.39), becomes

$$(k, N_\lambda\mp1, N_{\lambda'}\mp1|T_2^{(\mathrm{eff})}|i, N_\lambda, N_{\lambda'}) = D_\lambda^{(\pm)}D_{\lambda'}^{(\pm)}E_1^2W_{kj}W_{ji}\frac{[e^{\pm iq_{\lambda'}\cdot R_k}-e^{\pm iq_{\lambda'}\cdot R_j}][e^{\pm iq_\lambda\cdot R_j}-e^{\pm iq_\lambda\cdot R_i}]e^{i(\alpha_{kj}+\alpha_{ji})}}{(\epsilon_i-\epsilon_j)(\epsilon_j-\epsilon_k)(\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda+i\hbar s)}. \tag{1.47}$$

At this point it becomes expedient to examine the phonon phase factors of (1.47)—in particular, to compare them with those which are present in (1.44). From (1.47) one sees that these phase factors will occur in four possible combinations: $e^{i(\pm q_{\lambda'}\cdot R_j\pm iq_\lambda\cdot R_i)}$, $e^{i(\pm q_{\lambda'}\cdot R_k\pm q_\lambda\cdot R_j)}$, $e^{i(\pm q_{\lambda'}\cdot R_j\pm q_\lambda\cdot R_j)}$, $e^{i(\pm q_\lambda\cdot R_k\pm q_{\lambda'}\cdot R_i)}$. In order that the $T^{(1)}$ and $T^{(2)}$ amplitudes be capable of constructive interference, it is necessary for one or more of the phonon phase factors of one set to be coherent with one or more of the other; moreover, this coherence must be maintained under conditions in which (a) $\mathbf{q}_\lambda$ and $\mathbf{q}_{\lambda'}$ independently take on all possible directions, and (b) condition (II6) of Appendix II, namely,

$$\mathbf{q}_\lambda|\mathbf{R}_i-\mathbf{R}_j|\gg1, \tag{1.48}$$

is valid.

These coherence requirements are sufficiently severe so as to result in the jettisoning of most of the above-listed phonon phase factors, as will now be shown.

First of all, let us note that, since $\mathbf{R}_j$ does not occur in the phase factors of $T^{(1)}$, all the phase factors of $T^{(2)}$ which contain $\mathbf{R}_j$ cannot [by virtue of (1.48)] constructively interfere with those of $T^{(2)}$; the immediate consequence of this conclusion is that, of all the four factors listed for $T^{(2)}$, only $e^{i(\pm q_{\lambda'}\cdot R_k\pm q_\lambda\cdot R_i)}$ need be retained. It then follows, by virtue of (1.48), and the independent variability of $\mathbf{q}_\lambda$ and $\mathbf{q}_{\lambda'}$, that all terms of $T^{(1)}$ except those proportional to this same factor may be discarded. Applying this recipe to the expression obtained by substituting (1.39) into (1.44), one arrives at the result

$$(k, N_\lambda\mp1, N_{\lambda'}\mp1|T_1^{(\mathrm{eff})}|i, N_\lambda, N_{\lambda'}) = \frac{E_1^2D_\lambda^{(\pm)}D_{\lambda'}^{(\pm)}W_{ki}}{(\epsilon_i-\epsilon_j)(\epsilon_i-\epsilon_k)}\times e^{i(\pm q_{\lambda'}\cdot R_k\pm q_\lambda\cdot R_i)}e^{i\alpha_{ki}}. \tag{1.49}$$

By a similar procedure, the surviving term of (1.47) is found to be

$$(k, N_\lambda\mp1, N_{\lambda'}\mp1|T_2^{(\mathrm{eff})}|i, N_\lambda, N_{\lambda'}) = -\frac{E_1^2D_\lambda^{(\pm)}D_{\lambda'}^{(\pm)}W_{kj}W_{ji}}{(\epsilon_i-\epsilon_j)(\epsilon_j-\epsilon_k)(\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda+i\hbar s)}\times e^{i(\pm q_{\lambda'}\cdot R_k\pm q_\lambda\cdot R_i)}e^{i(\alpha_{kj}+\alpha_{ji})}. \tag{1.50}$$

(1.49) and (1.50) may now be superposed to yield for the *effective* two-stage transition amplitude the result

$$(k, N_\lambda\mp1, N_{\lambda'}\mp1|T^{(\mathrm{eff})}|i, N_\lambda, N_{\lambda'}) = -\frac{D_\lambda^{(\pm)}D_{\lambda'}^{(\pm)}e^{i(\pm q_{\lambda'}\cdot R_k\pm q_\lambda\cdot R_i)}}{(\epsilon_i-\epsilon_j)(\epsilon_j-\epsilon_k)}\times\left[e^{i\alpha_{ki}}W_{ki}+\frac{e^{i(\alpha_{kj}+\alpha_{ji})}W_{kj}W_{ji}}{\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda+i\hbar s}\right]. \tag{1.51}$$

The absolute square of (1.51), multiplied by $(2\pi/\hbar)\times\delta(\epsilon_i-\epsilon_k\pm\hbar\omega_\lambda\pm\hbar\omega_{\lambda'})$ gives the total two-stage transition probability $P^{(2)}(i, N_\lambda, N_{\lambda'}\to k, N_\lambda\mp1, N_{\lambda'}\mp1)$. The present work is, however, not concerned with this quantity, but only with that part $P_H^{(2)}(i, N_\lambda, N_{\lambda'}\to k, N_\lambda\mp1, N_{\lambda'}\mp1)$ which depends linearly on the magnetic field. This component is obtained by expanding the phase factors and picking out the terms linear in the phases, α_{ij}. With the additional use of the standard recipe,

$$1/(x+is)=P(1/x)-i\pi\delta(x), \tag{1.52}$$

one has

$$P_H^{(2)}(i, N_\lambda, N_{\lambda'}\to k, N_\lambda\mp1, N_{\lambda'}\mp1) = \frac{E_1^4|D_\lambda^{(\pm)}|^2|D_{\lambda'}^{(\pm)}|^2W_{kj}W_{ji}W_{ki}}{(\epsilon_i-\epsilon_j)^2(\epsilon_j-\epsilon_k)^2}\frac{e\mathbf{H}\cdot\mathbf{A}_{kji}}{\hbar c}\frac{(2\pi)^2}{\hbar}\times\delta(\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda)\delta(\epsilon_i-\epsilon_k\pm\hbar\omega_\lambda\pm\hbar\omega_{\lambda'}), \tag{1.53'}$$

[12] This point requires some further clarification. Namely, if the λ and λ' summations were each to extend over the whole lattice-vibration spectrum, the zeros of both energy denominators would be traversed. However, independent summation over λ and λ' is actually inappropriate, since it would count the same final state, $(k, N_\lambda\mp1, N_{\lambda'}\mp1)$, twice. A suitable nonredundant summation recipe is achieved by restricting, e.g., the λ' sum to values such that $\omega_{\lambda'}$ is either larger or smaller than ω_λ. If, for example $|\epsilon_i-\epsilon_j|<|\epsilon_j-\epsilon_k|$, and one wishes to retain (1.42), one imposes the condition $\omega_{\lambda'}>\omega_\lambda$. In that case, by virtue of (1.41) or (1.43), one may readily check that the energy denominator of the second term of (1.45), namely $\epsilon_i-\epsilon_j\pm\hbar\omega_{\lambda'}+i\hbar s$, cannot vanish, in accordance with the statement in the text. (If, on the other hand, $|\epsilon_i-\epsilon_j|>|\epsilon_j-\epsilon_k|$, one chooses the alternate recipe, $\omega_\lambda>\omega_{\lambda'}$, and arrives at the same result.)

or, more symmetrically,

$$P_H^{(2)}(i, N_\lambda, N_{\lambda'} \to k, N_\lambda \mp 1, N_{\lambda'} \mp 1) = \frac{E_1^4 |D_\lambda^{(\pm)}|^2 |D_{\lambda'}^{(\pm)}|^2 W_{kj} W_{ji} W_{ki}}{(\epsilon_i - \epsilon_j)^2 (\epsilon_j - \epsilon_k)^2} \frac{e\mathbf{H}\cdot\mathfrak{A}_{kji}}{\hbar c} \frac{(2\pi)^2}{\hbar} \times \delta(\epsilon_i - \epsilon_j \pm \hbar\omega_\lambda)\delta(\epsilon_j - \epsilon_k \pm \hbar\omega_{\lambda'}). \quad (1.53)$$

In obtaining (1.53′) or (1.53), use has been made of Eq. (1.35), in conjunction with (IIa) of Appendix II. In this connection, the sign of $\mathfrak{A}_{kji}$ is positive or negative according to whether the circuit $i \to j \to k \to i$ is counterclockwise or clockwise.

As stated above, $P_H^{(2)}(i, N_\lambda, N_{\lambda'}) \to k, N_\lambda \mp 1, N_{\lambda'} \mp 1)$ represents only part of the field-dependent jump probability. The other component originates from superpositions of the one-stage $(i, N_\lambda \to k, N_\lambda \mp 1)$ amplitude and those associated with various three-stage processes of the type $(i, N_\lambda, N_{\lambda'} \to i, N_\lambda \mp 1, N_{\lambda'} \to j, N_\lambda \mp 1, N_{\lambda'} \mp 1 \to k, N_\lambda \mp 1, N_{\lambda'})$, $(i, N_\lambda, N_{\lambda'} \to j, N_\lambda \mp 1, N_{\lambda'} \to j, N_\lambda \mp 1, N_{\lambda'} \mp 1 \to k, N_\lambda \mp 1, N_{\lambda'})$, etc.[13]

The amplitude of the one-stage process may be obtained from (1.39), and is

$$(k, N_\lambda \mp 1 | T_1 | i, N_\lambda) = E_1 D_\lambda^{(\pm)} \frac{W_{ki}}{\epsilon_i - \epsilon_k} e^{i\alpha_{ki}} \times [e^{\pm i\mathbf{q}_\lambda \cdot \mathbf{R}_k} - e^{\pm i\mathbf{q}_\lambda \cdot \mathbf{R}_i}]. \quad (1.54)$$

From the rather large number of conceivable three-stage processes, one has now the task of selecting those which are coherent with (1.54). This task is carried out in Appendix III, which also contains a detailed discussion of the various features relevant to coherence. The results of the treatment are contained in Eqs. (III3) and (III7), which give the two types of three-stage amplitudes capable of interfering with (1.54). These are

$$(k, N_\lambda \mp 1, N_{\lambda'} | T_3^{(k)} | i, N_\lambda \mp 1, N_{\lambda'}) = E_1^3 |D_{\lambda'}^{(\pm)}|^2 D_\lambda^{(\pm)} \times \frac{W_{kj} W_{ji} e^{i(\alpha_{kj} + \alpha_{ji})} e^{\pm i\mathbf{q}_\lambda \cdot \mathbf{R}_k}}{(\epsilon_i - \epsilon_j)^2 (\epsilon_i - \epsilon_k)(\epsilon_i - \epsilon_j \pm \hbar\omega_{\lambda'} + i\hbar s)}, \quad (1.55)$$

and

$$(k, N_\lambda \mp 1, N_{\lambda'} | T_3^{(i)} | i, N_\lambda \mp 1, N_{\lambda'} = -E_1^3 |D_{\lambda'}^{(\pm)}|^2 D_\lambda^{(\pm)} \times \frac{W_{kj} W_{ji} e^{i(\alpha_{kj} + \alpha_{ji})} e^{\pm i\mathbf{q}_\lambda \cdot \mathbf{R}_i}}{(\epsilon_i - \epsilon_k)(\epsilon_j - \epsilon_k)^2 (\epsilon_k - \epsilon_j \pm \hbar\omega_{\lambda'} + i\hbar s)}. \quad (1.56)$$

[13] It should be remarked here that the phonon modes λ and λ' are not the same as those involved in the previously discussed two-stage processes. In particular, the frequency ω_λ obeys the energy condition $\epsilon_i - \epsilon_k \pm \hbar\omega_\lambda = 0$.

It should here be mentioned that, since the λ' mode is involved only in intermediate states, and does not really appear in the final state (i.e., $N_\lambda \to N_{\lambda'}$), the total three-stage amplitude is to be obtained by summing over all λ', and over the two possibilities of absorption and emission. This summation will be deferred.

One has now to superpose (1.54) with (1.55) and (1.56), take the absolute square of the resultant,[14] and multiply by $(2\pi/\hbar)\delta(\epsilon_i - \epsilon_k \pm \hbar\omega_{\lambda'})$. As before, it is not the total result which is of interest, but only that part which varies linearly with the magnetic phase factors; the rest is therefore discarded. The result of this procedure is

$$P_H^{(3,1)}(i, N_\lambda \xrightarrow{N_{\lambda'} \mp 1} k, N_\lambda \mp 1) = \frac{(2\pi)^2}{\hbar} E_1^4 |D_\lambda^{(\pm)}|^2 |D_{\lambda'}^{(\pm)}|^2 W_{kj} W_{ji} W_{ki} \times \frac{e\mathbf{H}\cdot\mathfrak{A}_{kji}}{\hbar c} \left[\frac{\delta(\epsilon_i - \epsilon_k \pm \hbar\omega_\lambda)\delta(\epsilon_i - \epsilon_j \pm \hbar\omega_{\lambda'})}{(\epsilon_i - \epsilon_j)^2 (\epsilon_i - \epsilon_k)^2} + \frac{\delta(\epsilon_i - \epsilon_k \pm \hbar\omega_\lambda)\delta(\epsilon_k - \epsilon_j \pm \hbar\omega_{\lambda'})}{(\epsilon_j - \epsilon_k)^2 (\epsilon_i - \epsilon_k)^2} \right]. \quad (1.57)$$

Here, the superscript "(3,1)" has been used on the left-hand side as an indication of the number of stages of the contributing amplitudes. Also, the notation "$N_{\lambda'} \mp 1$" over the arrow indicates the intermediate participation of the λ' mode first in absorption (emission), then the reverse.

Upon adding (1.57) to (1.53) and summing over λ and λ' and the two possibilities of absorption and emission, one obtains, as the total magnetic field-dependent probability, the expression

$$P_H(i \to k) \sum_{\pm\lambda, \pm\lambda'} \frac{(2\pi)^2}{\hbar} E_1^4 |D_\lambda^{(\pm)}|^2 |D_{\lambda'}^{(\pm)}|^2 W_{kj} W_{ji} W_{ki} \times \frac{e\mathbf{H}\cdot\mathfrak{A}_{kji}}{hc} \left[\frac{\delta(\epsilon_i - \epsilon_k \pm \hbar\omega_\lambda)\delta(\epsilon_i - \epsilon_j \pm \hbar\omega_{\lambda'})}{(\epsilon_i - \epsilon_j)^2 (\epsilon_i - \epsilon_k)^2} + \frac{\delta(\epsilon_i - \epsilon_k \pm \hbar\omega_\lambda)\delta(\epsilon_k - \epsilon_j \pm \hbar\omega_{\lambda'})}{(\epsilon_i - \epsilon_k)^2 (\epsilon_j - \epsilon_k)^2} + \frac{\delta(\epsilon_i - \epsilon_j \pm \hbar\omega_\lambda)\delta(\epsilon_j - \epsilon_k \pm \hbar\omega_{\lambda'})}{(\epsilon_i - \epsilon_j)^2 (\epsilon_j - \epsilon_k)^2} \right], \quad (1.58)$$

wherein the double summation involves summing over the two possibilities of emission and absorption for each mode. Also, the delta functions of the last term have been changed from those in (1.53′) through the

[14] In carrying out this operation, use is made of condition (1.48) in that only amplitudes of similar phonon-dependent phase factors actually interfere.

use of the relation

$$\delta(x)\delta(x+y)=\delta(x)\delta(y). \tag{1.59}$$

It is now of interest to compare $P_H(i\to k)$ with the ordinary zeroth-order two-site jump probability, $P_0(i\to j)$, computed, e.g., by Miller and Abrahams.[3] This quantity is gotten by inserting (1.39) into the standard first-order perturbation expression. The result is

$$P'(i\to j)=\sum_{\pm\lambda}\frac{4\pi}{\hbar}E_1^2\,|D_\lambda^{(\pm)}|^2\frac{W_{ij}^2}{(\epsilon_i-\epsilon_j)^2}\times\delta(\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda), \tag{1.60}$$

wherein use has been made of (1.48) to discard cross-terms involving trigonometric functions of the argument $\mathbf{q}_\lambda\cdot(\mathbf{R}_j-\mathbf{R}_i)$.

It will now be noted that $P_H(i\to k)$ can be expressed in terms of the various $P_0(i\to j)$'s. In fact, upon comparing (1.58) and (1.60), one has, without further ado,

$$\begin{aligned}P_H(i\to k)&=\frac{\hbar}{4W_{ij}W_{jk}W_{ki}}\big[W_{jk}^2P_0(i\to k)P_0(i\to j)\\&\quad+W_{ki}^2P_0(i\to j)P_0(j\to k)\\&\quad+W_{ij}^2P_0(i\to k)P_0(k\to j)\big]\frac{e\mathbf{H}\cdot\mathfrak{A}_{kji}}{\hbar c}.\end{aligned} \tag{1.61}$$

For the purpose of the next section, it is desirable to formulate "reversibility" relationships between the various transition probabilities. It is first expedient to consider these relationships for the zeroth order two-site transition probabilities, $P_0(i\to j)$. Making use of the formula

$$N_\lambda+\tfrac{1}{2}\mp\tfrac{1}{2}=1/|1-e^{\pm\hbar\omega_\lambda/\kappa T}| \tag{1.62}$$

(which, as can readily be verified, holds for Planck's distribution) together with the energy restriction imposed by the delta function in (1.60), one has [upon substituting (1.39) into (1.60)]

$$\begin{aligned}P_0(i\to j)&=\sum_{\pm\lambda}=\frac{4\pi}{\hbar}E_1^2(\mathbf{q}_\lambda\cdot\mathbf{e}_\lambda)^2\left(\frac{\hbar}{2MN\omega_\lambda}\right)\\&\quad\times\frac{W_{ji}^2/(\epsilon_i-\epsilon_j)^2}{|1-e^{(\epsilon_i-\epsilon_j)/\kappa T}|}\delta(\epsilon_i-\epsilon_j+\hbar\omega_\lambda)\\&=Ze^{\epsilon_i/\kappa T}L_{ij},\end{aligned} \tag{1.63}$$

where

$$L_{ij}\equiv Z^{-1}\sum_{\lambda\pm}\frac{4\pi}{\hbar}E_1^2(\mathbf{q}_\lambda\cdot\mathbf{e}_\lambda)^2\left(\frac{\hbar}{2MN\omega_\lambda}\right)\times\frac{W_{ji}^2(\epsilon_i-\epsilon_j)^{-2}\delta(\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda)}{|e^{\epsilon_i/\kappa T}-e^{\epsilon_j/\kappa T}|} \tag{1.64}$$

is clearly symmetrical with respect to interchange of i and j, i.e.,

$$L_{ij}=L_{ji}, \tag{1.65}$$

and where

$$Z\equiv e^{-\epsilon_1/\kappa T}+e^{-\epsilon_2/\kappa T}+e^{-\epsilon_3/\kappa T}$$

is the three-site partition function. Inserting (1.63) into (1.61), one then has

$$\begin{aligned}P_H(i\to k)&=\frac{\hbar L_{ij}L_{ik}L_{ki}Z^2}{4W_{ij}W_{ik}W_{ki}}\left[\frac{W_{ik}^2}{L_{ik}}e^{2\epsilon_i/\kappa T}+\frac{W_{ki}^2}{L_{ki}}e^{(\epsilon_i+\epsilon_j)/\kappa T}\right.\\&\quad\left.+\frac{W_{ij}^2}{L_{ij}}e^{(\epsilon_i+\epsilon_k)/\kappa T}\right]e\mathbf{H}\cdot\mathfrak{A}_{kji}/\hbar c\\&\equiv\mathfrak{L}_{kji}Ze^{\epsilon_i/\kappa T},\end{aligned} \tag{1.66}$$

where

$$\begin{aligned}\mathfrak{L}_{kji}\equiv\frac{Z\hbar}{4}\frac{L_{ij}L_{ik}L_{kj}}{W_{ij}W_{ik}W_{kj}}&\left[\frac{W_{ik}^2}{L_{jk}}e^{\epsilon_i/\kappa T}+\frac{W_{ki}^2}{L_{ki}}e^{\epsilon_j/\kappa T}\right.\\&\left.+\frac{W_{ij}^2}{L_{ij}}e^{\epsilon_k/\kappa T}\right]\frac{e\mathbf{H}\cdot\mathfrak{A}_{kji}}{\hbar c}\end{aligned} \tag{1.67}$$

is readily seen[15] to be antisymmetric with respect to interchange of indices i, j, and k, i.e.,

$$\mathfrak{L}_{kji}=\mathfrak{L}_{ikj}=\mathfrak{L}_{jik}=-\mathfrak{L}_{ijk}=-\mathfrak{L}_{jki}=-\mathfrak{L}_{kij}. \tag{1.68}$$

II. ac HALL EFFECT

In Sec. I, explicit expressions were derived for the elementary jump-probabilities in the presence of a magnetic field. In the present section, these expressions will be applied to the study of electron-hopping in a three-site system in which, in addition to a dc magnetic field, there is also an applied oscillatory electric field. This case constitutes the simplest generalizations of the two-site problem treated by Pollak and Geballe[4] (in their analysis of their experimental results on ac impurity conduction) which is capable of yielding a nonvanishing Hall effect.

The basis of the treatment is a Boltzmann-type equation, of the form

$$\dot{}_i=\sum_{j\neq i}[P(j\to i)f_j-P(i\to j)f_i], \tag{2.1}$$

where i and j may both take on the values 1, 2, and 3 (subject, of course, to the condition $i\neq j$). Also,

$$P(i\to j)=P_0(i\to j)+P_H(i\to j),$$

where $P_0(i\to j)$ and $P_H(i\to j)$ are given by (1.63), (1.64), and (1.66), (1.67), respectively. Finally, the presence of the electric field $\mathbf{E}$ is taken into account implicitly in the site energies via the relation

$$\epsilon_i=\epsilon_i^{(0)}+e\mathbf{E}\cdot\mathbf{R}_i, \tag{2.2}$$

[15] The first two factors of (1.67) are obviously symmetric in the indices i, j, and k. The last factor is antisymmetric, in that the sign of $\mathfrak{A}_{kji}$ depends upon the sign of the rotation in the cycle $i\to j\to k\to i$.

where $\epsilon_i^{(0)}$ denotes the local energy in zero electric field (it corresponds to the ϵ_i of Sec. I).

It is expedient to introduce, in place of the f_i, new variables ϕ_i, defined by the relations

$$f_i=(1/Z)e^{-\beta\epsilon_i}(1+\phi_i), \tag{2.3}$$

where

$$\beta\equiv 1/\kappa T, \tag{2.4}$$

and

$$Z=e^{-\beta\epsilon_1}+e^{-\beta\epsilon_2}+e^{-\beta\epsilon_3} \tag{2.5}$$

is the partition function for a single electron (or, eventually, a hole) in the three-site system.

Substituting (2.3) into (2.1), and utilizing (1.63), (1.66), and (1.68), one has

$$Z^{-1}e^{-\beta\epsilon_1}\dot{\phi}_1+\frac{d}{dt}Z^{-1}e^{-\beta\epsilon_1}=-(L_{12}+L_{13})\phi_1+L_{12}\phi_2+L_{13}\phi_3 -\mathfrak{L}_{321}(\phi_2-\phi_3) \tag{2.6}$$

plus two other equations obtainable from (2.6) by cyclic permutation of the site indices.

A certain simplification of the left-hand side of (2.6) can be effected by so choosing the origin of the spatial coordinates so that

$$\exp(-\beta\epsilon_1^{(0)})\mathbf{R}_1+\exp(-\beta\epsilon_2^{(0)})\mathbf{R}_2 +\exp(-\beta\epsilon_3^{(0)})\mathbf{R}_3=0. \tag{2.7}$$

With this choice, one sees that (to first order in the impressed electric field)

$$\dot{\mathbf{E}}=Z^{-1}(-\beta e\dot{\mathbf{E}})\textstyle\sum_i \exp(-\beta\epsilon_i^{(0)})\mathbf{R}_i=0,$$

so that, with the additional assumption of harmonic time variation of $\mathbf{E}(\sim e^{-i\omega t})$, (2.6) becomes

$$Z^{-1}i\omega\beta e\mathbf{E}\cdot\mathbf{R}_1e^{-\beta\epsilon_1}=(i\omega Z^{-1}e^{-\beta\epsilon_1}-L_{12}-L_{13})\phi_1 +L_{12}\phi_2+L_{13}\phi_3-\mathfrak{L}_{321}(\phi_2-\phi_3), \tag{2.8}$$

wherein, and in what follows, ϵ_i will be written in place of $\epsilon_i^{(0)}$, and will denote the zero-electric-field value of the local energy of the ith site.

For convenience in subsequent algebra, let us introduce the notations

$$\mathbf{r}_i=\mathbf{R}_ie^{-\beta\epsilon_i}Z^{-1}, \tag{2.9}$$

$$\omega_i=\omega e^{-\beta\epsilon_i}Z^{-1}, \tag{2.10}$$

$$\mathfrak{L}=\mathfrak{L}_{321}. \tag{2.11}$$

Equation (2.8), together with the two obtained therefrom by cyclic permutation of site indices, then take the form

$$(i\omega_1-L_{12}-L_{13})\phi_1+(L_{12}-\mathfrak{L})\phi_2+(L_{13}+\mathfrak{L})\phi_3 =i\omega\mathbf{r}_1\cdot\beta e\mathbf{E}, \tag{2.12a}$$

$$(L_{21}+\mathfrak{L})\phi_1+(i\omega_2-L_{23}-L_{21})\phi_2+(L_{23}-\mathfrak{L})\phi_3 =i\omega\mathbf{r}_2\cdot\beta e\mathbf{E}, \tag{2.12b}$$

$$(L_{31}-\mathfrak{L})\phi_1+(L_{32}+\mathfrak{L})\phi_2+(i\omega_3-L_{31}-L_{32})\phi_3 =i\omega\mathbf{r}_3\cdot\beta e\mathbf{E}. \tag{2.12c}$$

Concurrently, (2.7) may be written as

$$\mathbf{r}_1+\mathbf{r}_2+\mathbf{r}_3=0. \tag{2.13}$$

The solution of (2.12) is considerably facilitated by the circumstance that, as is readily verified, the determinant of the coefficients

$$\Delta\equiv\begin{vmatrix} i\omega_1-L_{12}-L_{13} & L_{12}-\mathfrak{L} & L_{13}+\mathfrak{L} \\ L_{12}+\mathfrak{L} & i\omega_2-L_{23}-L_{21} & L_{23}-\mathfrak{L} \\ L_{31}-\mathfrak{L} & L_{32}+\mathfrak{L} & i\omega_3-L_{31}-L_{32}\end{vmatrix} \tag{2.14}$$

depends quadratically on $\mathfrak{L}$. For the purposes of the present paper, in which only effects linear in the magnetic field are of interest, this quadratic dependence may be ignored, i.e., Δ may be approximated by its zero-field ($\mathfrak{L}=0$) value. It then follows that the ϕ_i obtained from the solution of Eqs. (2.12) will have the form

$$\phi_i=\phi_i^{(0)}+\phi_i^{(H)}, \tag{2.15}$$

where the $\phi_i^{(0)}$ are independent of $\mathfrak{L}$ (and hence of magnetic field) and the $\phi_i^{(H)}$ are linear in $\mathfrak{L}$. Since only the latter are of interest, as far as the Hall effect is concerned, they alone will be considered. One finds, by straight-forward algebra,

$$\phi_1^{(H)}=-\omega\mathfrak{L}\Delta^{-1}\beta e\mathbf{E}\cdot(\mathbf{r}_2\omega_3-\mathbf{r}_3\omega_2), \tag{2.16a}$$

$$\phi_2^{(H)}=-\omega\mathfrak{L}\Delta^{-1}\beta e\mathbf{E}\cdot(\mathbf{r}_3\omega_1-\mathbf{r}_1\omega_3), \tag{2.16b}$$

$$\phi_3^{(H)}=-\omega\mathfrak{L}\Delta^{-1}\beta e\mathbf{E}\cdot(\mathbf{r}_1\omega_2-\mathbf{r}_2\omega_1). \tag{2.16c}$$

Knowing the $\phi_i^{(H)}$, one may compute the (magnetic) field-induced component of electric current. It is given by

$$\mathbf{j}^{(H)}\equiv -e\textstyle\sum_i \mathbf{R}_i\dot{f}_i=-(i\omega/Z)e\sum_i \mathbf{R}_ie^{-\beta\epsilon_i}\phi_i^{(H)} =-i\omega\textstyle\sum_i \mathbf{r}_i\phi_i^{(H)} \tag{2.17}$$

[the last two equalities holding by virtue of (2.3) and (2.9)]. Substituting (2.16) into (2.17), one has

$$\mathbf{j}^{(H)}=i\omega^2e^2\Delta^{-1}\beta\mathbf{E}\cdot[(\mathbf{r}_2\omega_3-\mathbf{r}_3\omega_2)\mathbf{r}_1 +(\mathbf{r}_3\omega_1-\mathbf{r}_1\omega_3)+(\mathbf{r}_1\omega_2-\mathbf{r}_2\omega_1)\mathbf{r}_3] =i\omega^2e^2\Delta^{-1}\beta\mathbf{E}\cdot[(\omega_1+\omega_2+\omega_3)(\mathbf{r}_2\mathbf{r}_1-\mathbf{r}_1\mathbf{r}_2)], \tag{2.18}$$

the last equality resulting from the use of (2.13) and some algebraic manipulation.

It is now of interest to average $\mathbf{j}^{(H)}$ over all orientations of the triangular configuration, i.e., over all values of $\mathbf{r}_1$ and $\mathbf{r}_2$, subject to the restriction that the magnitudes of these vectors and the angle between them remain constant. In carrying out this average, it is necessary to take account of the dependence of $\mathfrak{L}$ on orientation. Referring back to (1.67), one sees that

this dependence is essentially of the form[16]

$$\mathfrak{L}=\mathfrak{L}_0\frac{(\mathbf{r}_2\times\mathbf{r}_1)\cdot\mathbf{H}}{|\mathbf{r}_2\times\mathbf{r}_1|} \tag{2.19}$$

where $\mathfrak{L}_0=\mathfrak{L}_{321}{}^{(0)}$ differs from (1.67) in that the scalar product $\mathbf{H}\cdot\mathfrak{A}_{321}$ is replaced by $\mathfrak{A}_{321}$.

Inserting (2.19) into (2.18) and simplifying the square bracket, one has

$$\begin{aligned}\mathbf{j}^{(H)}&=\frac{i\omega^2e^2\mathfrak{L}_0\beta\mathbf{H}}{\Delta}\cdot\frac{(\mathbf{r}_2\times\mathbf{r}_1)}{|\mathbf{r}_2\times\mathbf{r}_1|}[\mathbf{r}_2\mathbf{r}_1\cdot\mathbf{E}-\mathbf{r}_1\mathbf{r}_2\cdot\mathbf{E}](\omega_1+\omega_2+\omega_3)\\&=\frac{i\omega^2e^2\mathfrak{L}_0\beta\mathbf{H}}{\Delta}\cdot\frac{(\mathbf{r}_2\times\mathbf{r}_1)}{|\mathbf{r}_2\times\mathbf{r}_1|}[(\mathbf{r}_2\times\mathbf{r}_1)\times\mathbf{E}](\omega_1+\omega_2+\omega_3).\end{aligned} \tag{2.20}$$

The average of (2.20) over orientations is clearly equivalent to its average over all directions of the vector cross-product, $\mathbf{r}_2\times\mathbf{r}_1$; one has [with subsequent use of (2.9)]

$$\begin{aligned}\mathbf{j}^{(H)}&=\frac{i\omega^2e^2\mathfrak{L}_0\beta}{\Delta}\left(\frac{\omega_1+\omega_2+\omega_3}{3}\right)|\mathbf{r}_2\times\mathbf{r}_1|\,(\mathbf{H}\times\mathbf{E})\\&=i\omega^2e^2\mathfrak{L}_0\beta|\mathbf{R}_2\times\mathbf{R}_1|\left(\frac{\omega_1+\omega_2+\omega_3}{3}\right)\\&\qquad\times e^{-\beta(\epsilon_1+\epsilon_2)}Z^2\Delta(\mathbf{H}\times\mathbf{E}).\end{aligned} \tag{2.21}$$

Now, the area of the triangle defined by the geometrical centers of the three sites is

$$\begin{aligned}A_{321}&=\tfrac{1}{2}|(\mathbf{R}_2-\mathbf{R}_1)\times(\mathbf{R}_3-\mathbf{R}_1)|\\&=\tfrac{1}{2}|\mathbf{R}_2\times\mathbf{R}_1|\,(1+e^{\beta(\epsilon_3-\epsilon_1)}+e^{\beta(\epsilon_3-\epsilon_2)}),\end{aligned}$$

the last equality holding by virtue of (2.7). Comparing (2.21) and (2.22), one then has

$$\begin{aligned}\mathbf{j}^{(H)}&=\frac{2i\omega^3e^2\mathfrak{L}_0\beta}{Z^3\Delta}\times\left(\frac{\omega_1+\omega_2+\omega_3}{3}\right)A_{321}\\&\qquad\times e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}(\mathbf{H}\times\mathbf{E}).\end{aligned} \tag{2.22}$$

At this point, it is desirable to introduce a simplification also employed by Pollak and Geballe. This simplification consists in replacing the various Boltzmann factors $e^{-\beta\epsilon_i}$ by unity. It would appear to be a reasonable approximation, provided that

$$\kappa T\gtrsim|\epsilon_i-\epsilon_j|. \tag{2.23}$$

In this "high-temperature" case, the procedure should certainly be adequate for order-of-magnitude estimates of $\mathbf{j}^{(H)}$. Since the present study is concerned primarily with such estimates (rather than with precise, quantitative results) the procedure of replacing each $e^{-\beta\epsilon_i}$ by unity will be followed without further ado. The result is

$$\mathbf{j}^{(H)}=\frac{2i\omega^3e^2\mathfrak{L}_0\beta}{Z_\infty{}^4\Delta_\infty}A_{321}(\mathbf{H}\times\mathbf{E}), \tag{2.24}$$

where

$$Z_\infty=3, \tag{2.25}$$

and where the determinant Δ_∞ [the limiting form of (2.14)] as $e^{-\beta\epsilon}\to1$ ($\omega_i\to Z_\infty{}^{-1}\omega$) becomes, upon expanding and discarding of terms in $\mathfrak{L}^2$,

$$\begin{aligned}\Delta_\infty=i\omega Z_\infty{}^{-3}[&-\omega^2-2i\omega(l_1+l_2+l_3)\\&+3(l_1l_2+l_1l_3+l_2l_3)],\end{aligned} \tag{2.26}$$

the notation

$$l_1\equiv Z_\infty L_{23},\quad l_2=Z_\infty L_{13},\quad l_3=Z_\infty L_{12} \tag{2.27}$$

having been introduced for convenience of writing.

At this point, it is desirable to exhibit explicitly the dependence of the "Hall-probability coefficient" $\mathfrak{L}_0$ on the two-site probability coefficients $l_k\equiv ZL_{ij}$. This dependence becomes simple in the above-introduced high-temperature approximation, $e^{-\beta\epsilon_i}Z^{-1}\to Z_\infty{}^{-1}$, for which the L_{ij}, as given by (1.64), reduce to

$$L_{ij}=Z_\infty{}^{-1}\kappa TW_{ji}{}^2B, \tag{2.28}$$

where

$$B\equiv\sum_{\pm\lambda}\frac{4\pi}{\hbar}E_1{}^2(\mathbf{q}_\lambda\cdot\mathbf{e}_\lambda)^2\left(\frac{\hbar^2}{2MN}\right)\frac{\delta(\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda)}{(\hbar\omega_\lambda)^4} \tag{2.29}$$

[use having been made of the delta function to replace $(\epsilon_i-\epsilon_j)^2$ by $(\hbar\omega_\lambda)^2$]. In the case of sufficiently low $|\epsilon_i-\epsilon_j|$ (compared to the Debye energy), one may use the further approximation

$$\omega_\lambda=c_\lambda|\mathbf{q}_\lambda|, \tag{2.30}$$

where c_λ depends only on the direction of $\mathbf{q}_\lambda$ (and on the particular vibrational branch under consideration). Introducing the replacements

$$\sum_\lambda(\cdots)=\frac{V}{8\pi^3}\sum_j(\cdots)d^3q=\frac{V}{8\pi^3}\sum_j\int\int(\cdots)q^2dqd\Omega,$$

(where V is the volume of the sample, $d\Omega$ and element of solid angle in $\mathbf{q}$ space, and $j=1$, 2, or 3 designates a particular one of three acoustical branches), one then has, upon integrating with respect to q

$$B=\frac{1}{2\pi^2\hbar}E_1{}^2\frac{1}{2\rho\hbar^3}\sum_j\int c_j{}^{-5}(\mathbf{n}\cdot\mathbf{e}_j)^2d\Omega \tag{2.31}$$

[16] The basic assumption involved in (2.19) is that the vector direction of the effective flux area, $\mathfrak{A}_{321}$, coincides with the direction of the geometrical area, $\mathbf{R}_2\times\mathbf{R}_1/|\mathbf{R}_2\times\mathbf{R}_1|=\mathbf{r}_2\times\mathbf{r}_1/|\mathbf{r}_2\times\mathbf{r}_1|$. This coincidence certainly obtains when the term $V_a(\mathbf{r})$ in Eq. (1.26) is negligible. Moreover, even when this term is taken into account, it is only its asymmetry with respect to reflection through the plane of the triangle which could tilt the direction of $\mathfrak{A}_{321}$ with respect to that of the geometrical area. It appears quite reasonable to assume that such an asymmetry vanishes on the average.

(where ρ is the mass density and $\mathbf{n}$ a unit vector in the $\mathbf{q}$ direction). By virtue of the fact that c_j is a function of $\mathbf{n}$ alone, (2.31) clearly depends only on properties of the host crystal (mainly elastic).

Introducing (2.28) into (1.67), and again replacing Boltzmann exponentials by unity, one has

$$\mathfrak{L}_{\kappa ji}=\frac{3\hbar}{4}Z_\infty^{\frac{1}{3}}(L_{ij}L_{jk}L_{ki})^{\frac{1}{3}}(\kappa TB)^{\frac{1}{2}}\frac{e(\mathbf{H}\cdot\mathfrak{A}_{\kappa ji})}{\hbar c},$$

which, by virtue of (2.27) and the remark subsequent to (2.19), is equivalent to

$$\mathfrak{L}_0=\frac{3\hbar}{4Z_\infty}(\kappa T)^{\frac{1}{3}}B^{\frac{1}{2}}\frac{e\mathfrak{A}_{321}}{\hbar c}(l_1l_2l_3)^{\frac{1}{3}}. \tag{2.32}$$

Substituting (2.32) and (2.26) into (2.24) (and remembering that $\beta\equiv 1/\kappa T$), one then has

$$\mathbf{j}^{(Z)}=\left[\frac{2\omega^2e^2}{Z_\infty^2(\kappa T)^{\frac{1}{3}}}\frac{3\hbar}{4}\frac{B^{\frac{1}{2}}e}{\hbar c}\mathfrak{A}_{321}A_{321}\right]\mathbf{H}\times\mathbf{E}$$
$$\times\frac{(l_1l_2l_3)^{\frac{1}{3}}}{-\omega^2-2i\omega(l_1+l_2+l_3)+3(l_1l_2+l_1l_3+l_2l_3)}. \tag{2.33}$$

In what follows, attention will be focussed principally in the imaginary component of $\mathbf{j}^{(H)}$, i.e., the one 90° out of phase with the electric field. This quantity, after a little algebra, can be put into the form

$$\mathbf{j}_i^{(H)}=\frac{2e^2}{Z_\infty^2(\kappa T)^{\frac{1}{3}}}\frac{3\hbar}{4}\frac{B^{\frac{1}{2}}e}{\hbar c}\mathfrak{A}_{321}A_{321}(\mathbf{H}\times\mathbf{E})\frac{2\omega^3(l_1l_2l_3)^{\frac{1}{3}}(l_1+l_2+l_3)}{\omega^4+\omega^2[3(l_1^2+l_2^2+l_3^2)+(l_1+l_2+l_3)^2]+9(l_1l_2+l_1l_3+l_2l_3)^2}. \tag{2.34}$$

As contrasted with the real component, (2.34) attains a maximum when the l's are all in the neighborhood of ω; this feature will be utilized in summing $j_i^{(H)}$ over all possible 3-site configurations, an operation which is carried out immediately below.

The principal variable involved in the summation are the mutual distances R_{12}, R_{13}, and R_{23}, between the three sites. These distances enter into (2.34) principally via their effect on the l's, i.e., on the L_{ij} (via the dependence of the W_{ij} on R_{ij}). At this stage, rather than entering upon an evaluation of the W_{ij}, as given by Eq. (I13) of Appendix I, one may conveniently utilize an expression given by Pollak and Geballe[4] [their Eq. (13a)], which they in turn obtain from the theory of Miller and Abrahams.[3] The quoted expression reads (in the notation of the present paper)

$$L_{ij}=Z^{-1}C(R_{ij}/a)^{\frac{1}{2}}e^{-2R_{ij}/a}, \tag{2.35}$$

where a is the radius of the donor wave function and C a numerical constant, which for silicon has the value

$$C=1.65\times10^{12}T\ \text{sec}^{-1} \tag{2.36}$$

(T being expressed in degrees Kelvin[17]).

One has now to compute the occurrence-probability distribution of the R_{ij} over all possible three-site configurations. Selecting, e.g., site 1 as a reference point, one may readily write down the probability, $W(R_{12})dR_{12}$, that a second site (site 2) be so situated that its distance from the first lies between R_{12} and $R_{12}+dR_{12}$; it is

$$W(R_{12})dR_{12}=4\pi N_DR_{12}^2dR_{12}, \tag{2.37}$$

where N_D is the density of donor sites.[18]

With respect to the third site, it is necessary to specify not only its distance, R_{13}, from site 1, but also the angle θ_{23}, between $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$. One readily obtains

$$W(R_{13},\theta_{23})dR_{13}d(\cos\theta_{23})=2\pi N_DR_{13}^2dR_{13}d\cos\theta_{23},$$

which, by virtue of the relationship

$$R_{23}^2=R_{12}^2+R_{12}^2-2R_{12}R_{13}\cos\theta_{23} \tag{2.38}$$

may be written as

$$W(R_{13},R_{23})dR_{13}dR_{23}=2\pi N_D(R_{13}R_{23}/R_{12})dR_{13}dR_{23}. \tag{2.39}$$

Combining (2.39) with (2.37), one obtains the occurrence distribution for all the R_{ij}, namely,

$$W(R_{12},R_{13},R_{23})dR_{12}dR_{13}dR_{23}=8\pi^2N_D^2R_{12}R_{13}R_{23}dR_{12}dR_{13}dR_{23}. \tag{2.40}$$

Combining (2.40) with (2.35) and introducing the notation

$$r_k\equiv R_{ij} \tag{2.41}$$

(i.e., $r_1\equiv R_{23}$, $r_2\equiv R_{13}$, $r_3\equiv R_{12}$), one has for the occurrence distribution of the $l_\kappa\equiv L_{ij}$,

$$W(l_1,l_2,l_3)dl_1dl_2dl_3=8\pi^2N_D^2r_1r_2r_3dr_1dr_2dr_3$$
$$=\frac{8\pi^2N_D^2a^3}{8}r_1r_2r_3\pi_i\left(\frac{1-3a}{4r_i}\right)^{-1}\frac{dl_1}{l_1}\frac{dl_2}{l_2}\frac{dl_3}{l_3}, \tag{2.42}$$

[17] It may be noted in passing that (2.35) incorporates the effect of mass-anisotropy of the conduction band of the host crystal; for the simple isotropic case actually considered in this paper, the factor $(R_{ij}/a)^{\frac{1}{2}}$ would be replaced by a term proportional to $(R_{ij}/a)^2$. The use of (2.35) is more appropriate for numerical estimation, in view of the fact that impurity conduction experiments have been carried out principally with Ge and Si samples.

[18] Strictly speaking, one should introduce the restriction that no other site lie closer than R_{12}. This restriction would have the effect of multiplying (2.37) by the "exclusion" factor, $\exp(-4\pi N_DR_{12}^3/3)$. In what follows, as in the work of Pollak and Geballe,[4] the distances of interest turn out to be rather smaller than the critical cutoff distance $\sim(3/4\pi N_D)^{\frac{1}{3}}$ at which the exponential factor becomes important. Physically, this means that the intersite distances of the configurations which provide the principal contribution to the current (both ordinary and Hall) are less than the average distance between donors; for such configurations, the likelihood of an additional site being still closer to either of the two (or three) already under consideration, is remote and may be ignored.

where the product goes over the values $i=1, 2, 3$, and where r_i is that value which satisfied (2.35), i.e.,

$$l_i=C(r_i/a)^{\frac{1}{2}}e^{-2r_i/a}. \tag{2.35}$$

Introducing (2.42) into (2.34), together with the transformations

$$l_i\equiv\omega\xi_i^2,$$

one has

$$\mathbf{j}_i^{(H)}=\frac{4e^2\omega^{\frac{3}{2}}}{Z_\infty^2(\kappa T)^{\frac{1}{2}}}\frac{3\hbar}{4}\frac{B^{\frac{1}{2}}e}{\hbar c}(\mathbf{H}\times\mathbf{E})8\pi^2a^3N_D^2\int_0^\infty\int_0^\infty\int_0^\infty \mathfrak{A}_{321}\pi_i\left\{\frac{r_i}{1-3a/4r_i}\right\}$$
$$\times\frac{(\xi_1^2+\xi_2^2+\xi_3^2)d\xi_1d\xi_2d\xi_3}{1+[3(\xi_1^4+\xi_2^4+\xi_3^4)+(\xi_1^2+\xi_2^2+\xi_3^2)^2]+9(\xi_1^2\xi_2^2+\xi_1^2\xi_3^2+\xi_2^2\xi_3^2)^2}, \tag{2.43}$$

where, in place of (2.35), one has

$$\omega\xi_i^2/C=(r_i/a)^{\frac{1}{2}}e^{-r_i/a}. \tag{2.44}$$

A considerable simplification is achieved by approximating the r_i's in the factors, $r_i/(1-3a/4r_i)$, by a single constant value, r_0, which is given by (2.43) with each ξ_i^2 set equal to unity, i.e., by the solution of the equation

$$\omega/C=(r_i/a)^{\frac{1}{2}}e^{-2r_0/a}. \tag{2.45}$$

This approximation is based (a) on the circumstance that the r_i's are rather slowly-varying (logarithmic) functions of the ξ_i, and (b) the anticipation that the main contributions to (2.43) will come from regions in which the ξ_i are of the order of unity.

In a similar spirit, the area factors $\mathfrak{A}_{321}$ and A_{321} will both be replaced by the area of the equilateral triangle whose three sides are equal to r_0, as given by (2.45). Thus

$$\mathfrak{A}_{321}\rightarrow A_{321}\rightarrow\sqrt{3}r_0^2/4.$$

With these approximations, one then has for the magnitude of $\mathbf{j}_i^{(H)}$

$$\frac{j_i^{(H)}}{E}=\frac{4e^2\omega^{3/2}}{Z_\infty^2(\kappa T)^{\frac{1}{2}}}\frac{3\hbar}{4}B^{\frac{1}{2}}\frac{eH}{\hbar c}\left(\frac{\sqrt{3}r_0^2}{2}\right)^2\frac{r_0^3}{(1-3a/4r_0)^3}8\pi^2a'N_D\mathcal{J}, \tag{2.46}$$

where

$$\mathcal{J}\equiv\int_0^\infty\int_0^\infty\int_0^\infty\frac{(\xi_1^2+\xi_2^2+\xi_3^2)d\xi_1d\xi_2d\xi_3}{1+[3(\xi_1^4+\xi_2^4+\xi_3^4)+(\xi_1^2+\xi_2^2+\xi_3^2)^2]+9(\xi_1^2\xi_2^2+\xi_1^2\xi_3^2+\xi_2^2\xi_3^2)^2}$$
$$=\int_{\text{octant}}d\Omega\int_0^\infty\frac{\xi^4d\xi}{1+\xi^4[1+3(n_1^4+n_2^4+n_3^4)]+9\xi^8(n_1^2n_2^2+n_1^2n_3^2+n_2^2n_3^2)^2}. \tag{2.47}$$

In (2.47), $\xi^2=\xi_1^2+\xi_2^2+\xi_3^2$ and $n_i\equiv\xi_i/\xi$ are the direction cosines of the vector (ξ_1,ξ_2,ξ_3) in a Cartesian space; in the last equality the angle integration goes over the octant for which the n_i are all positive.

An approximate evaluation of the dimensionless quantity $\mathcal{J}$ is carried out in Appendix IV. The result is [cf. Eq. (IV8)], $\mathcal{J}\geqq 0.62$. Inserting this result into (2.46) and multiplying by the density of charge carriers [which may be taken equal to the minority (acceptor) concentration, N_A], one obtains (as a lower limit) the following expression for the imaginary component of Hall conductivity

$$\sigma_i^{(H)}=\frac{N_Aj_i^{(H)}}{E}=\frac{(3)(0.70)e^2\omega^{3/2}\hbar}{Z_\infty^2(\kappa T)^{\frac{1}{2}}}B^{\frac{1}{2}}\left(\frac{\sqrt{3}r_0^2}{4}\right)^2$$
$$\times\frac{eH}{\hbar c}\frac{r_0^3}{(1-3a/4r_0)^3}8\pi^2a^3N_D^2N_A. \tag{2.54}$$

It is desirable to express this result in terms of a quantity analogous to the Hall angle. Because of the ready availability of a formula for the real part of the ordinary rf conductivity σ_r, namely, Eq. (15) of Pollak and Geballe,[4] which reads[19]

$$\sigma_r=\frac{\pi}{3}N_AN_D\frac{e^2}{\kappa T}\frac{r_0^4a}{2}\frac{\pi}{2}\omega, \tag{2.55}$$

where

$$r_0=14.8-\tfrac{1}{2}\ln\omega$$

[as computed by Pollak and Geballe from equations equivalent to (2.45) and (2.36) of this paper] the "equivalent Hall angle" will be defined as

$$\theta_i^{(H)}\equiv\sigma_i^{(H)}/\sigma_r. \tag{2.56}$$

[19] The arc-tangent term of the square-bracket of Pollak and Geballe's Eq. (15) is herewith ignored, in accordance with the procedure of these authors.

Dividing (2.54) by (2.55), and setting $Z_\infty=3$, one has (with neglect terms $\sim a/r_0$)

$$\theta_i^{(H)}=9.80(N_D a^2 r_0)(\hbar^2\omega\kappa TB)^{\frac{1}{3}}\alpha_H, \tag{2.57}$$

where

$$\alpha_H\equiv\sqrt{3}r_0^2eH/4\hbar c \tag{2.58}$$

is the "magnetic" phase shift associated with an equilateral triangular configuration (in which the three intersite distances are all equal to r_0), and where the quantity B is given by (2.31). The latter relation is expediently simplified by the standard assumptions that (a) the lattice-vibration modes may be considered either as transverse or longitudinal, and (b) the longitudinal velocity is taken to be a constant, c_l. Eq. (2.31) then reduces to

$$B=E_1^2/\pi\rho\hbar^4c_l^5, \tag{2.59}$$

which, when substituted into (2.57), yields

$$\theta_i^{(H)}=9.80(N_D a^2 r_0)(\hbar\omega\kappa TE_1^2/\pi\rho^3c_l^5)^{\frac{1}{3}}\alpha_H. \tag{2.60}$$

An estimate of the numerical value of $\theta_i^{(H)}$ as given by (2.60) will now be carried out for the case of phosphorus-doped silicon (under the conditions prevailing in the experiments of Pollak and Geballe[9]). Numerical values of the relevant parameters are taken as $\rho=2.42$ g/cm^3, $c_l=9\times10^5$ cm/sec, $E_1=6$ ev; donor wave-function radius $a=20$ A (as quoted by Pollak and Geballe). The quantity r_0 depends upon temperature and frequency. At e.g., 10°K and $\omega=2\pi\times10^5$ sec^{-1}, $r_0\sim10a=2\times10^{-6}$ cm. For N_D a representative value of 10^{16} cm^{-3} will be used. Finally α_H is set equal to[20] $\frac{1}{2}$.

With these values (2.60) gives

$$\theta_i^{(H)}=0.62\times10^{-6}. \tag{2.61}$$

An alternate way of describing the magnitude of the Hall effect is in terms of the Hall mobility. In analogy with the dc case, let us define the ac Hall mobility—more specifically, its imaginary part— by the relation

$$\theta_i^{(H)}\equiv\mu_i^{(H)}H/c. \tag{2.62}$$

From (2.62), (2.60), and (2.58), one has

$$\mu_i^{(H)}=[9.80(N_D a^2 r_0^3)\sqrt{3}e/4\hbar]\times(\hbar\omega\kappa TE_1^2/\pi\rho\hbar^3c_l^5)^{\frac{1}{3}}. \tag{2.63}$$

One may now compare (2.63) with the (real part of the) ac drift mobility [obtained by dividing (2.55) by eN_A], i.e.,

$$\mu_r^{(D)}=\frac{\pi}{3}N_D\frac{e}{\kappa T}\frac{r_0^4a}{2}\frac{\pi}{2}\omega. \tag{2.64}$$

The ratio is

$$\frac{\mu_i^{(H)}}{\mu_r^{(D)}}=\frac{5.15a}{r_0}\left(\frac{\kappa T}{\hbar\omega}\right)\left(\frac{\hbar\omega\kappa TE_1^2}{\pi\rho\hbar^3c_l^5}\right)^{\frac{1}{3}}. \tag{2.65}$$

[20] This value corresponds to $r_0=2\times10^{-6}$ cm and $H=20\,000$ gauss.

Using the numerical values given in the text previous to Eq. (2.61) for the various parameters, one finds

$$\mu_i^{(H)}/\mu_r^{(D)}=191\gg1. \tag{2.66}$$

It is thus seen that the Hall mobility is actually much larger than the drift mobility. This result appears to be characteristic of hopping-type conduction mechanisms in low-mobility materials, in which (as in the present paper) the dominant Hall-conductivity mechanism involves the interactions between *three* sites. In particular, the result $\mu^{(H)}/\mu^{(D)}\gg1$ has been obtained[1] for small-polaron hopping conduction, in those cases wherein the crystallographic arrangement favors the three-site mechanism.[21]

Unfortunately, from the experimental point of view, the numerically favorable situation exhibited by (2.66) is rather illusory. In particular, even though the Hall field (specifically, its imaginary component)

$$E_i^{(H)}=(1/N_Aec)(\mu_i^H/\mu_r^D)J^{(r)}H \tag{2.67}$$

is large compared to the so-called "normal" value, $J^{(r)}H/N_Aec$, the resistivities of the materials under consideration are extremely large ($\sim10^9$ ohm cm) (cf. reference 4). What one is actually measuring is a change (due to the magnetic field) of the transverse conductivity, which, according to (2.62), is some 10^{-6} times smaller than the ordinary conductivity and hence $\sim10^{-15}$ ohm^{-1} cm^{-1}. Such conductivities are small indeed.

It should however be remarked that the above numerical estimates of ordinary conductivity and Hall angle relate to conditions prevailing in an experiment (that of Pollak and Geballe[4]), which was not designed to measure Hall currents. It is to be hoped that the exploitation of a number of possibilities (such as more highly doped samples, and/or larger ac electric fields) may yield the sensitivity required for an experimental check of the theory.

III. SIGN OF THE HALL COEFFICIENT

In this section the sign of the Hall effect will be discussed. It should be remarked at the outset that the discussion will apply only to the case of large compensation, in which the number of electrons on donor sites is small compared to the total number of donors—this case, strictly speaking, is the one for which the theory has been developed.

Referring back to the end of Sec. I, one sees [cf. (1.66) and (1.67)] that if, say, a three-site circuit $i\rightarrow j\rightarrow k\rightarrow i$ is counterclockwise and if the component

[21] Such arrangements are characterized by the feature that each site has two nearest neighbors which are also nearest neighbors of each other (e.g., face-centered cubic). On the other hand, structures such as body-centered or simple cubic, in which a closed path connecting nearest-neighbor sites contains a minimal number of four sites, yield Hall mobilities which are considerably smaller than those provided by the three-site mechanism and which, for representative values of the parameters, are comparable in magnitude to the drift mobilities.

of the field parallel to the normal of the enclosed area is positive (i.e., $\mathbf{H}\cdot\mathfrak{A}_{kji}>0$), the sign of $P_H(i\rightarrow k)$ coincides with that of $W_{ij}W_{jk}W_{ki}$. If, as will be argued below, the W_{ji} are all negative, it follows that $P_H(i\rightarrow k)$ is negative. Moreover, according to (1.66) and (1.68), $P_H(i\rightarrow j)=-P_H(i\rightarrow k)$ and is therefore positive. It is then clear that, in the presence of a magnetic field, $P(i\rightarrow k)$ and $P(i\rightarrow j)$ decrease and increase, respectively, thereby providing a net flow of electrons from k to j. Since the nonmagnetic zeroth order electron current is, on the average, directed from i to some point between j and k, the Hall angle is *negative*, as might perhaps be expected for electrons.

It remains to justify the above assertion that the W_{ji} are negative. The sign of a typical W_{ji} is determined by that of the "transfer potential" function $w_{ji}(\mathbf{r})$ [given by Eq. (1.12)] in an ellipsoidal region containing the sites i and j, in which $u(\mathbf{r}-\mathbf{R}_i)u(\mathbf{r}-\mathbf{R}_j)$ is maximal. The principal term in (1.12) is contained in the first parentheses; it is the one which appears in all overlap calculations, and is obviously negative in the intersite region. For the case of a hydrogenic ground-state wave function, its contribution to W_{ji} is known to be $-2e^2/\kappa R_{ij}S_{ji}$ [cf. H. Bethe, *Handbuch der Physik* **24**, 1 (1933), especially p. 539].

Turning now to the other terms in $w_{ji}(\mathbf{r})$, one notes that they each represent differences between the value of a potential function at $\mathbf{r}$ and an equally weighted average of its values at sites i and j. These differences will generally fluctuate in sign in such a way as to yield relatively small net contributions of the form $(\gamma e^2/\kappa R_{ik})S_{ji}$ and $(\gamma' e^2/\kappa R_{ia})S_{ji}$, where R_{ia} is the distance from site i to the nearest acceptor ion and where (as indicated by sample calculations) γ and γ' may be expected to be small fractions of unity (apart from exceptional cases in which, e.g., the acceptor ion is abnormally close to one of the two donor sites under consideration).

If the above (admittedly crude) estimate of the magnitudes of the different contributions to W_{ji} be accepted (it may here be remarked that Miller and Abrahams[3] discard the second and third terms in (1.12) entirely), it follows that W_{ji} is negative; from the above discussion, one then concludes that the Hall coefficient itself is negative.

APPENDIX I

In this appendix, the atomic orbital approximation to the eigenfunctions of the three-site electronic Hamiltonian,

$$H_e=T+V_a(\mathbf{r})-\frac{e^2}{\kappa}\times\left[\frac{1}{|\mathbf{r}-\mathbf{R}_1|}+\frac{1}{|\mathbf{r}-\mathbf{R}_2|}+\frac{1}{|\mathbf{r}-\mathbf{R}_3|}\right], \quad \text{(I1)}$$

will be developed. The standard projection procedure consists in substituting the general atomic-orbital expression

$$\psi(\mathbf{r})=\textstyle\sum_i C_i\phi_i(\mathbf{r}) \quad \text{(I2)}$$

into Schrödinger's equation, multiplying on the left by a particular ϕ_j, and integrating over $\mathbf{r}$. Taking cognizance of the fact that the isolated donor functions, ϕ_i, are solutions of the equations

$$\left(T-\frac{e^2}{\kappa|\mathbf{r}-\mathbf{R}_i|}\right)\phi_i(\mathbf{r})=E_d\phi_i(\mathbf{r}) \quad \text{(I3)}$$

with E_d the negative of the donor ionization energy), one obtains the three equations ($j=1, 2, 3$)

$$E\textstyle\sum_i T_{ji}C_i=\sum_i H_{ji}C_i, \quad \text{(I4)}$$

where

$$T_{ji}=\delta_{ji}+S_{ji}, \quad \text{(I5)}$$

$$S_{ji}=\left(1-\delta_{ji}\int\phi_j^*\phi_i dV\right), \quad \text{(I6)}$$

$$H_{ji}=E_dT_{ji}+U_{ji}, \quad \text{(I7)}$$

$$U_{ji}=\int\phi_j^*(\mathbf{r})\left[V_a(\mathbf{r})-\frac{e^2}{\kappa}\sum_{k\neq i}\frac{1}{|\mathbf{r}-\mathbf{R}_k|}\right]\phi(_i\mathbf{r})dV. \quad \text{(I8)}$$

It is now expedient to multiply both sides of (I4) by the matrix T_{ij}^{-1}, inverse to T_{ji}; then, upon summing over the intermediate index j, and going over to the approximation

$$T_{lj}^{-1}\cong\delta_{lj}-S_{lj} \quad \text{(I9)}$$

(applicable when the nonorthogonality integrals S_{ij} are small compared to unity, as will here be assumed), one has

$$(E-E_d)C_l=\sum_i\left[U_{li}-\sum_{j\neq l}S_{lj}U_{ji}\right]C_i \cong\sum_i\left[U_{li}-S_{li}U_{ii}\right]C_i \quad \text{(I10)}$$

(the last approximate equality holding by virtue of the relative smallness of the terms, $\sum_{j\neq l}S_{lj}W_{ji}$, which involve squares of overlap integrals). Equation (I10) may more conveniently be written in the form

$$(E-\epsilon_l)C_l=\sum_{i\neq l}J_{li}C_i, \quad \text{(I11)}$$

where

$$\epsilon_i=E_d+U_{ii}$$

$$=E_d+\int|\phi_i(\mathbf{r})|^2\left[V_a(\mathbf{r})-\sum_{k\neq i}\frac{e^2}{\kappa|\mathbf{r}-\mathbf{R}_k|}\right]dV, \quad \text{(I12)}$$

and

$$J_{ji}=U_{ji}-S_{ji}U_{ii}$$

$$=\int\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})\left[V_a(\mathbf{r})-\sum_{k\neq i}\frac{e^2}{\kappa|\mathbf{r}-\mathbf{R}_k|}\right]dV -S_{ji}U_{ii}. \quad \text{(I13)}$$

As in the treatment of Miller and Abrahams,[2] it will here be assumed that the differences in the "local energies", ϵ_i, are large compared to the "transfer energies" J_{ij}. In this case (I11) may be solved by standard Rayleigh-Schrödinger perturbation theory. The result, to first order in J_{ij}, is

$$C_i^{(\alpha)}=\delta_{i\alpha}+\frac{J_{i\alpha}}{\epsilon_\alpha-\epsilon_i}(1-\delta_{i\alpha}). \tag{I14}$$

Inserting this result into (I2), one obtains for the eigenstates ψ_α of H_e the result

$$\psi_\alpha=\phi_\alpha+\sum_{i\neq\alpha}\phi_i\frac{J_{i\alpha}}{\epsilon_\alpha-\epsilon_i}, \tag{I15}$$

or, more explicitly[22]

$$\psi_1=\phi_1+\frac{J_{21}}{\epsilon_1-\epsilon_2}\phi_2+\frac{J_{31}}{\epsilon_1-\epsilon_3}\phi_3, \tag{I16a}$$

$$\psi_2=\frac{J_{12}}{\epsilon_2-\epsilon_1}\phi_1+\phi_2+\frac{J_{32}}{\epsilon_2-\epsilon_3}\phi_3, \tag{I16b}$$

$$\psi_3=\frac{J_{13}}{\epsilon_3-\epsilon_1}\phi_1+\frac{J_{23}}{\epsilon_3-\epsilon_2}\phi_2+\phi_3. \tag{I16c}$$

It is now desirable to transform relation (I13) for J_{ji} into a form which will be more useful for the extended treatment. Adding and subtracting the term $(U_{ii}+U_{jj})/2$ to the right-hand side and analyzing the first equality of (I12), one has

$$J_{ji}=\int\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})\left[V_a(\mathbf{r})-\sum_{k\neq i}\frac{e^2}{\kappa|\mathbf{r}-\mathbf{R}_k|}-\frac{U_{ii}+U_{jj}}{2}\right]dV-(\epsilon_i-\epsilon_j)S_{ji}/2. \tag{I17}$$

Further simplification is achieved by taking advantage of the fact that, in all cases of interest, the radii of the donor wave functions are small compared to intersite distances. Under such conditions, U_{ii} is well approximated by the formula

$$U_{ii}=V_a(\mathbf{R}_i)-\sum_{k\neq i}\frac{e^2}{\kappa|\mathbf{R}_i-\mathbf{R}_k|}, \tag{I18}$$

which, when inserted into (I17), yields

$$J_{ji}=\int\phi_j^*(\mathbf{r})\phi_i(\mathbf{r})w_{ji}(\mathbf{r})dV-(\epsilon_i-\epsilon_j)S_{ji}/2, \tag{I19}$$

where

$$w_{ji}(\mathbf{r})\equiv\left(V_a(\mathbf{r})-\frac{V_a(\mathbf{R}_i)+V_a(\mathbf{R}_j)}{2}\right)-\frac{e^2}{\kappa}\left(\frac{1}{|\mathbf{r}-\mathbf{R}_j|}-\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|}\right)-\frac{e^2}{\kappa}\left(\frac{1}{|\mathbf{r}-\mathbf{R}_k|}-\frac{\frac{1}{2}}{|\mathbf{R}_i-\mathbf{R}_k|}-\frac{\frac{1}{2}}{|\mathbf{R}_j-\mathbf{R}_k|}\right). \tag{I20}$$

APPENDIX II

In this appendix, the matrix elements of electron-lattice interaction

$$(j|H_{\text{int}}|i)=E_1\int\psi_j^*(\mathbf{r})\eta(\mathbf{r})\psi_i(\mathbf{r})dV \tag{II1}$$

will be evaluated. From the form of $\eta(\mathbf{r})$ given in Eq. (1.5), it is clear that (II1) consists of a superposition of matrix elements of the form

$$A_{ji}^{(\lambda)}\equiv\int\psi_j^*e^{i\mathbf{q}_\lambda\cdot\mathbf{r}}\psi_i dV. \tag{II2}$$

Attention will therefore be focussed on these quantities.

A guiding principle of the calculation is that, in view of the basic assumptions

$$J_{ji}/|\epsilon_i-\epsilon_j|\ll 1;\quad S_{ji}\ll 1,$$

the nonvanishing terms of only the lowest order in the J_{ij} and S_{ij} need be retained. Thus, in the case of the diagonal matrix elements, $A_{ii}^{(\lambda)}$, it is sufficient to approximate each ψ_i by the corresponding ϕ_i, so that

$$A_{ii}^{(\lambda)}=\int|\phi_i|^2e^{i\mathbf{q}_\lambda\cdot\mathbf{r}}dV.$$

Following the procedure of Miller and Abrahams,[3] one may in addition assume that the q_λ of interest obey the condition

$$q_\lambda a\ll 1 \tag{II3}$$

(where a is the radius of a donor wave function); it then follows that

$$A_{ii}^{(\lambda)}=e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_i}. \tag{II4}$$

For the evaluation of the off-diagonal elements $A_{ji}^{(\lambda)}$ it is necessary to go to the first order in J_{ji} and S_{ji}. Thus, one has, e.g., for

$$A_{21}^{(\lambda)}=\frac{J_{21}}{\epsilon_1-\epsilon_2}e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_2}+\frac{J_{12}^*}{\epsilon_2-\epsilon_1}e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_1}+\int\phi_2^*e^{i\mathbf{q}_\lambda\cdot\mathbf{r}}\phi_1 dV. \tag{II5}$$

[22] The orthogonality (to first order in the J_{ij}) of the ψ's may be verified directly, if one takes account of the fact that the J_{ij} are not Hermitian, but obey the relation $J_{ij}-J_{ji}^*=S_{ij}[\epsilon_i-\epsilon_j]$.

At this point, another approximation utilized by Miller and Abrahams will be introduced. It is, namely, that the distance between donor sites, $|\mathbf{R}_i-\mathbf{R}_j|$, is large enough so that, for the q_λ of interest, the condition

$$q_\lambda|\mathbf{R}_i-\mathbf{R}_j|\gg 1 \tag{II6}$$

is obeyed. (Obviously, the condition can be satisfied for sufficiently low donor concentrations.) With the aid of (II6), one may show that the third term of (II5), namely,

$$K_{12}{}^{(\lambda)}\equiv\int\phi_2{}^*e^{i\mathbf{q}_\lambda\cdot\mathbf{r}}\phi_1 dV,$$

is small compared to the others.[23] It will therefore be discarded in what follows.

Introducing Eq. (1.23) into (II5), one has

$$A_{21}{}^{(\lambda)}=\frac{W_{21}}{\epsilon_1-\epsilon_2}\left[e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_2}-e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_1}\right]e^{i\alpha_{21}} -\tfrac{1}{2}S_{21}e^{-\beta_{21}}\left[e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_2}+e^{i\mathbf{q}_\lambda\cdot\mathbf{R}_1}\right]. \tag{II7}$$

In obtaining (II7), use has been made of the relationships

$$\alpha_{ij}=-\alpha_{ji}, \tag{II8a}$$

$$\beta_{ij}=-\beta_{ji}, \tag{II8b}$$

$$W_{ij}=W_{ji}, \tag{II8c}$$

$$S_{ij}=S_{ji}, \tag{II8d}$$

which may, in turn, be verified directly from the text relations[24] (1.24)-(1.29) (and which, incidentally, must be valid in order that the ψ_i remain orthogonal in the presence of the magnetic field). The insertion of (II2) and the cyclic permutations of (II7) into the expression

$$(j|H_{\rm int}|i)=iE_1\sum_\lambda \mathbf{q}_\lambda\cdot\mathbf{e}_\lambda\left(\frac{\hbar}{2MN\omega_\lambda}\right)^{\frac{1}{2}} \times(b_\lambda A_{ji}{}^{(\lambda)}-b_\lambda{}^*A_{ji}{}^{(\lambda)\dagger}) \tag{II9}$$

yields the desired matrix elements of electron-lattice interaction.

APPENDIX III

In this appendix, the selection of those three-stage processes whose amplitudes are coherent with that of (1.54) will be carried out. This selection is governed by a number of conditions. One first notes (condition 1) that, since the final lattice state differs from the initial in that only a single phonon belonging to the λ mode has been absorbed or emitted ($N_\lambda\rightarrow N_\lambda\mp 1$), one of the three stages must involve this process, the other two must have to do with the absorption and re-emission (or emission and reabsorption) of phonons of another mode ($N_{\lambda'}\rightarrow N_{\lambda'}\mp 1\rightarrow\cdots\rightarrow N_{\lambda'}$).

Secondarily (condition 2), it is necessary that the energy of one of the two intermediate states coincide with (i.e., be contained in a continuum which overlaps) the energy of the initial state. This requirement is needed in order that the net zero-field phase difference of the two interfering amplitudes be $\pm 90°$ (as discussed in connection with the two-stage interferences [in particular in the text between Eqs. (1.45) and (1.46)]).

Finally (condition 3), it is necessary [by virtue of inequality (1.48)] that the "phonon" phase factors of the three-stage amplitudes coincide with one of those given by Eq. (1.54), i.e., they must reduce to either $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k}$ or $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_i}$. These three conditions will now be used to select the relevant three-stage processes.

A

Let us begin by looking for those processes whose amplitudes are proportional to $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k}$. Since the λ mode is (by condition 1) to be involved in only one stage, it is necessary that (in going from i to j to k) the λ mode participate either in the transition $j\rightarrow k$, or in a "diagonal transition", $k\rightarrow k$. The other stages, in particular diagonal transitions on either i or j, or transitions $i\rightarrow j$, must "use" another λ' mode.

The initial process could conceivably be diagonal ($i, N_{\lambda'}\rightarrow i, N_{\lambda'}\mp 1$) giving rise to a phase factor $e^{\pm i\mathbf{q}_{\lambda'}\cdot\mathbf{R}_i}$. Since this phase factor does not occur in the net three-stage amplitude, it would have to get eliminated in the next stage, which would hence be of the type ($i, N_{\lambda'}\mp 1\rightarrow j, N_\lambda$), to be followed by ($j, N_\lambda\rightarrow k, N_\lambda\mp 1$). This possibility, however, would violate condition 2, in that the two successive intermediate states would have energies which differ from the initial by $\pm\hbar\omega_\lambda$ and $\epsilon_j-\epsilon_i$, respectively. It then follows that the first stage must be of the form ($i, N_{\lambda'}\rightarrow j, N_{\lambda'}\mp 1$). Furthermore, from the phonon phase factor ($e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_j}$

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[23] The reason is that the domain over which the magnitude of $\phi_2{}^*\phi_1$ is of the order of its maximum value, is a prolate ellipsoid with minor axis $\sim(a|\mathbf{R}_2-\mathbf{R}_1|)^{\frac{1}{2}}$ and major axis $\sim|\mathbf{R}_1-\mathbf{R}_2|/2$. Over this domain, the oscillations of the factor $e^{i\mathbf{q}_\lambda\cdot\mathbf{r}}$ cause destructive interference.

[24] This verification is straightforward except for the α_{ij}. In this case, it turns out that $\varrho_{ji}{}^{(1)}$, as given by the text relation (1.26), is not equal to $\varrho_{ij}{}^{(1)}$. However, it will be noted that the difference between, say, $\varrho_{ji}{}^{(1)}$ and the obviously symmetrical quantity

$$\mathbf{P}_{ji}{}^{(S)}\equiv W_{ji}{}^{-1}\int u(\mathbf{r}-\mathbf{R}_j)u(\mathbf{r}-\mathbf{R}_i)\left[\frac{w_{ji}(\mathbf{r})+w_{ij}(\mathbf{r})}{2}\right]\mathbf{r}dV$$

is given by [cf. Eq. (1.20) of Appendix I]

$$\Delta\varrho_{ji}{}^{(1)}=W_{ji}{}^{-1}\int u(\mathbf{r}-\mathbf{R}_j)u(\mathbf{r}-\mathbf{R}_i)\left[\frac{e^2}{2\kappa}\frac{1}{|\mathbf{r}-\mathbf{R}_i|}-\frac{e^2}{2\kappa|\mathbf{r}-\mathbf{R}_j|}\right]\mathbf{r}dV,$$

which, in view of the symmetry of the donor functions, and of the term in square brackets, has the form

$$\Delta\varrho_{ji}{}^{(1)}=A_{ji}\mathbf{R}_i+B_{ji}(\mathbf{R}_j-\mathbf{R}_i),$$

where $A_{ji}=A_{ij}$ and $B_{ji}=B_{ij}$ are certain constants. With this form it is seen that

$$\varrho_{ji}{}^{(1)}-\varrho_{ij}{}^{(1)}=\Delta\varrho_{ji}{}^{(1)}-\Delta\varrho_{ij}{}^{(1)} =A_{ji}(\mathbf{R}_i-\mathbf{R}_j)+2B_{ji}(\mathbf{R}_j-\mathbf{R}_i)=C_{ji}(\mathbf{R}_j-\mathbf{R}_i),$$

which clearly makes no contribution to the triple scalar product in the text relation (1.25), which defines α_{ji}.

$-e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_i}$) in the matrix element [cf. text equation (1.39)] only the first term, $e^{\pm i\mathbf{q}_{\lambda'}\cdot\mathbf{R}_j}$, is to be retained. (The other phase-factor, $e^{\pm i\mathbf{q}_{\lambda'}\cdot\mathbf{R}_i}$, could never be cancelled out in the second or third stage, since site i will not participate in them.)

Coming to the second stage, there are the two possibilities of a diagonal ($j\rightarrow j$) or a nondiagonal ($j\rightarrow k$) transition. These will be considered in sequence.

(1) The diagonal ($j\rightarrow j$) transition cannot use the λ mode; by virtue of condition 1, which requires that this mode occur only once, its use must be reserved for the transition involving site k (so as to provide the phase factor $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k}$). The diagonal transition must therefore be

$$(j, N_{\lambda'}\mp 1\rightarrow j, N_{\lambda'}).$$

It then follows that for this case, the total sequence of transitions is

$$(i, N_\lambda, N_{\lambda'}\rightarrow j, N_\lambda, N_{\lambda'}\mp 1\rightarrow j, N_\lambda, N_{\lambda'}\rightarrow k, N_\lambda\mp 1, N_{\lambda'}).$$

[One notes that the second intermediate state has the same lattice quantum numbers as the initial, so that it is necessarily virtual (with energy differing from the initial state by the amount, $\epsilon_j-\epsilon_i$).] The amplitude for this three-stage process may now be written down, and is[25]

$$(k, N_\lambda\mp 1, N_{\lambda'}|T_3^{(1)}|i, N_\lambda\mp 1, N_{\lambda'}) = E_1^3|D_{\lambda'}{}^{(\pm)}|^2 D_\lambda{}^{(\pm)} \times\frac{W_{kj}W_{ji}e^{i(\alpha_{kj}+\alpha_{ji})}e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k}}{(\epsilon_i-\epsilon_j)(\epsilon_j-\epsilon_k)(\epsilon_i-\epsilon_j\pm\hbar\omega_{\lambda'}+i\hbar s)(\epsilon_i-\epsilon_j)}. \quad \text{(III1)}$$

(2) Let us now consider the remaining possibility for the second stage, namely a transition of the type ($j, N_{\lambda'}\mp 1\rightarrow k, N_{\lambda'}$). The final stage is then necessarily diagonal, of the form[26] ($k, N_\lambda\rightarrow k, N_\lambda\mp 1$). The total sequence of transitions is thus

$$(i, N_\lambda, N_{\lambda'}\rightarrow j, N_\lambda, N_{\lambda'}\mp 1\rightarrow k, N_\lambda, N_{\lambda'}\rightarrow k, N_\lambda\mp 1, N_{\lambda'},$$

the associated amplitude is

$$(k, N_\lambda\mp 1, N_{\lambda'}|T_3^{(2)}|i, N_\lambda\mp 1, N_{\lambda'}) = E_1^3|D_{\lambda'}{}^{(\pm)}|^2 D_\lambda{}^{(\pm)} \times\frac{W_{kj}W_{ji}e^{i(\alpha_{kj}+\alpha_{ji})}e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k}}{(\epsilon_i-\epsilon_j)(\epsilon_j-\epsilon_k)(\epsilon_i-\epsilon_j\pm\hbar\omega_{\lambda'}+i\hbar s)(\epsilon_i-\epsilon_k)}, \quad \text{(III2)}$$

wherein the energy of the first intermediate state is [as in the case of (III1)] required to lie in the immediate vicinity of the initial energy, since that of the second intermediate state necessarily differs by the amount $\epsilon_k-\epsilon_i$.

The superposition of (III1) and (III2) yields

$$(k, N_\lambda\mp 1, N_{\lambda'}|T_3^{(k)}|i, N_\lambda\mp 1, N_{\lambda'}) = E_1^3|D_{\lambda'}{}^{(\pm)}|^2 D_\lambda{}^{(\pm)} \times\frac{W_{kj}W_{ji}e^{i(\alpha_{kj}+\alpha_{ji})}e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k}}{(\epsilon_i-\epsilon_j)^2(\epsilon_i-\epsilon_k)(\epsilon_i-\epsilon_j\pm\hbar\omega_{\lambda'}\pm i\hbar s)}, \quad \text{(III3)}$$

wherein the superscript "(k)" is used to indicate the fact that the phonon phase factor is a function of the position $\mathbf{R}_k$ of the kth site.

B

Let us now consider the other contributing three-stage processes; according to the remarks at the beginning of this appendix, they must be such as to exhibit eventual proportionality to $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_i}$ (and to no other phonon phase factor).

In order to realize the factor $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_i}$, it is necessary that the λ mode participate in either the first or second stages of the transition, since only factors of the form $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_j}$ or $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k}$ could be generated in the third stage. If the λ mode participates in the second stage, the transition must still involve the ith site, i.e., hence, the first transition would have to be of the diagonal form ($i, N_{\lambda'}\rightarrow i, N_{\lambda'}\mp 1$), giving rise to the phase factor $e^{\pm i\mathbf{q}_{\lambda'}\cdot\mathbf{R}_i}$. The required cancellation of this phase factor would have to occur in the next (second) transition, which would therefore have to be of the form ($i, N_{\lambda'}\mp 1\rightarrow j, N_{\lambda'}$) contrary to hypothesis. It therefore follows that the λ mode *must* participate in the *first* stage. This stipulation still permits two choices, either diagonal ($i, N_\lambda\rightarrow i, N_\lambda\mp 1$) or nondiagonal ($i, N_\lambda\rightarrow j, N_\lambda\mp 1$); these will now be considered in order.

(1) With the first transition of the type ($i, N_\lambda\rightarrow i, N_\lambda\mp 1$), the remaining two must be (in sequence) ($i, N_\lambda\mp 1, N_{\lambda'}\rightarrow j, N_\lambda\mp 1, N_{\lambda'}\mp 1\rightarrow k, N_\lambda\mp 1, N_{\lambda'}$). Let us here observe that the first intermediate state is virtual; in fact, from footnote 13, the associated energy denominator, $\mp\hbar\omega_\lambda$, may be set equal to $\epsilon_k-\epsilon_i$. It then follows that the second energy denominator,

$$\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda\mp\hbar\omega_{\lambda'}+i\hbar s=\epsilon_k-\epsilon_j\pm\hbar\omega_{\lambda'}+i\hbar s,$$

must be of the "resonance" type, in which the continuum of intermediate energies overlaps the initial energy, thus requiring[27]

$$\epsilon_k-\epsilon_j\pm\hbar\omega_{\lambda'}=0. \quad \text{(III4)}$$

[25] In accordance with the above remarks, the relevant terms of the first, second, and third stages are those whose phonon phase factors are $e^{\pm i\mathbf{q}_{\lambda'}\cdot\mathbf{R}_j}$, $e^{\pm i\mathbf{q}_{\lambda'}\cdot\mathbf{R}_j}$, and $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_q}$, respectively.

[26] An alternate order of phonon mode participation (for the second and third stages) such as

$$(j, N_{\lambda'}\mp 1, N_\lambda\rightarrow k, N_{\lambda'}\mp 1, N_\lambda\mp 1\rightarrow k, N_{\lambda'}, N_\lambda\mp 1)$$

would yield terms proportional to

$$e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_j}(e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k}-e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_j})e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_k},$$

and hence incapable of interference with (1.54).

[27] The λ' mode is here obviously different from that participating in (III 3). As will be seen later, this difference is inconsequential, since the two types of amplitudes will never interfere.

The net amplitude of the above described three-stage transition may now be written down, and is

$$(k, N_\lambda \mp 1, N_{\lambda'}|T_3^{(3)}|i, N_\lambda, N_{\lambda'}) = -E_1^3|D_{\lambda'}{}^{(\pm)}|^2 D_\lambda{}^{(\pm)} \times \frac{W_{kj}W_{ji}e^{i(\alpha_{kj}+\alpha_{ji})}e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_i}}{(\epsilon_i-\epsilon_j)(\epsilon_j-\epsilon_k)(\epsilon_k-\epsilon_i)(\epsilon_k-\epsilon_j\pm\hbar\omega_{\lambda'}+i\hbar s)}. \quad \text{(III5)}$$

(2) Assuming the first transition to be of the nondiagonal type $(i, N_\lambda \to j, N_\lambda \mp 1)$, one must then take the second transition to be diagonal. Otherwise, one would have $(i, N_\lambda, N_{\lambda'} \to j, N_\lambda \mp 1, N_{\lambda'} \to k, N_{\lambda'} \mp 1, N_{\lambda'} \mp 1 \to k, N_\lambda \mp 1, N_{\lambda'})$ in which, by virtue of footnote 13 (and the basic presumptions $\epsilon_i \neq \epsilon_j \neq \epsilon_k$), both energy denominators are nonvanishing. One is thus left with

$$(i, N_\lambda, N_{\lambda'} \to j, N_\lambda \mp 1, N_{\lambda'} \to j, N_\lambda \mp 1, N_{\lambda'} \mp 1 \to k, N_\lambda \mp 1, N_{\lambda'}),$$

in which the energy denominator of the second intermediate state, namely,

$$\epsilon_i-\epsilon_j\pm\hbar\omega_\lambda\pm\hbar\omega_{\lambda'}+i\hbar s=\epsilon_k-\epsilon_j\pm\hbar\omega_{\lambda'}+i\hbar s$$

is of the resonance form, as long as (III4) is satisfied. The net amplitude for this transition is

$$(k, N_\lambda \mp 1, N_{\lambda'}|T_3^{(4)}|i, N_\lambda, N_{\lambda'}) = E_1^3|D_{\lambda'}{}^{(\pm)}|^2 D_\lambda{}^{(\pm)} \times \frac{W_{kj}W_{ji}e^{i(\alpha_{kj}+\alpha_{ji})}e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_i}}{(\epsilon_i-\epsilon_j)(\epsilon_j-\epsilon_k)(\epsilon_k-\epsilon_j)(\epsilon_k-\epsilon_j\pm\hbar\omega_{\lambda'}+i\hbar s)}, \quad \text{(III6)}$$

wherein use has been made of footnote 13 in rewriting the first energy denominator. The superposition of (III5) and (III6) yields

$$(k, N_\lambda \mp 1, N_{\lambda'}|T_3^{(i)}|i, N_\lambda, N_{\lambda'}) = -E_1^3|D_{\lambda'}{}^{(\pm)}|^2 D_\lambda{}^{(\pm)} \times \frac{W_{kj}W_{ji}e^{i(\alpha_{kj}+\alpha_{ji})}e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_i}}{(\epsilon_i-\epsilon_k)(\epsilon_j-\epsilon_k)^2(\epsilon_k-\epsilon_j\pm\hbar\omega_{\lambda'}+i\hbar s)}, \quad \text{(III7)}$$

wherein the superscript "(i)" has been used on the left-hand side to denote the fact that the phonon-dependent factor, $e^{\pm i\mathbf{q}_\lambda\cdot\mathbf{R}_i}$, depends on the location of the ith site.

APPENDIX IV

In this appendix the dimensionless quantity,

$$\mathcal{J}=\int_{\text{octant}} d\Omega \int_0^\infty \frac{\xi^4 d\xi}{1+\xi^4[1+3(n_1^4+n_2^4+n_3^4)]+9\xi^8(n_1^2n_2^2+n_1^2n_3^2+n_2^2n_3^2)^2}, \quad \text{(IV1)}$$

given by the last equality of (2.47) will be evaluated. Here, as pointed out in the text subsequent to (2.47), the $n_i=\xi_i/\xi$ are direction cosines in a Cartesian space, and $\xi^2\equiv\xi_1^2+\xi_2^2+\xi_3^2$.

The integration over ξ may first be performed; the result is

$$\mathcal{J}=\int_{\text{octant}} \pi 2^{-\frac{1}{4}}\left[\frac{1}{(3-b)^{\frac{1}{2}}}\frac{1}{\{1+b+[8(b-1)]^{\frac{1}{2}}\}^{\frac{1}{4}}+\{1+b-[8(b-1)]^{\frac{1}{2}}\}^{\frac{1}{4}}} \times \frac{1}{\{1+b+[8(b-1)]^{\frac{1}{2}}\}^{\frac{1}{4}}+\{1+b-[8(b-1)]^{\frac{1}{2}}\}^{\frac{1}{4}}}\right] d\Omega,$$

where

$$b=3(n_1^4+n_2^4+n_3^4). \quad \text{(IV2)}$$

The integrand of the expression for $\mathcal{J}$ can be simplified considerably by use of the algebraic relations

$$\{1+b+[8(b-1)]^{\frac{1}{2}}\}^{\frac{1}{2}}+\{1+b-[8(b-1)]^{\frac{1}{2}}\}^{\frac{1}{2}}=8^{\frac{1}{2}}, \quad \text{(IV3a)}$$

$$\{1+b+[8(b-1)]^{\frac{1}{2}}\}^{\frac{1}{4}}+\{1+b-[8(b-1)]^{\frac{1}{2}}\}^{\frac{1}{4}} =2^{\frac{1}{4}}[2^{\frac{1}{2}}+(3-b)^{\frac{1}{2}}]^{\frac{1}{4}} \quad \text{(IV3b)}$$

(each of which is readily verified by squaring both sides of the relation in question). One obtains

$$\mathcal{J}=\frac{\pi}{(4)2^{\frac{1}{4}}}\int_{\text{octant}}\left[\frac{1}{(3-b)^{\frac{1}{2}}}\frac{1}{[2^{\frac{1}{2}}+(3-b)^{\frac{1}{2}}]^{\frac{1}{2}}}\right] d\Omega, \quad \text{(IV4)}$$

which, from (IV2) and use of the relation

$$1-n_1^2+n_2^2+n_3^2$$

may be written as

$$\mathcal{J}=\frac{\pi}{(8)3^{\frac{1}{4}}}\int_{\text{octant}}\frac{1}{[n_1^2n_2^2+n_1^2n_3^2+n_2^2n_3^2]^{\frac{1}{2}}} \times \frac{d\Omega}{[1+3(n_1^2n_2^2+n_1^2n_3^2+n_2^2n_3^2)^{\frac{1}{2}}]^{\frac{1}{2}}}. \quad \text{(IV5)}$$

At this point, the approximation of replacing the quantity, $[1+3^{\frac{1}{2}}(n_1^2n_2^2+n_1^2n_3^2+n_2^2n_3^2)^{\frac{1}{2}}]^{\frac{1}{2}}$ by its maxi-

mum, namely $2^{\frac{1}{2}}$, will be introduced. One then has

$$\mathcal{J}\geqq\mathcal{J}_m\equiv\frac{\pi}{8(6)^{\frac{1}{2}}}\int_{\text{octant}}\frac{d\Omega}{[n_1^2n_2^2+n_1^2n_3^2+n_2^2n_3^2]^{\frac{1}{2}}}$$
$$=\frac{\pi}{8(6)^{\frac{1}{2}}}\int_0^{\pi/2}\int_0^{\pi/2}\frac{d\theta d\phi}{[\cos^2\theta+\frac{1}{4}\sin^2\theta\sin^2 2\phi]^{\frac{1}{2}}},\quad\text{(IV6)}$$

where θ and ϕ are polar and azimuthal angles, respectively.

The integration over θ now gives

$$\mathcal{J}_m=\frac{\pi}{8(6)^{\frac{1}{2}}}\int_0^{\pi/2}K[(1-\tfrac{1}{4}\sin^2\psi)^{\frac{1}{2}}]d\psi,\quad\text{(IV7)}$$

where $\psi\equiv 2\phi$, and where

$$K(k)=\int_0^{\pi/2}\frac{d\theta}{(1-k^2\sin^2\theta)^{\frac{1}{2}}}$$

is a standard elliptic integral.

To proceed further, it is useful to express $K(k)$ as a series in ascending powers of the argument

$$k'=(1-k^2)^{\frac{1}{2}}=\tfrac{1}{2}\sin\psi.$$

One has (cf. Jahncke and Emde, *Tables of Functions*, (Dover Publications, Inc., New York, 1945) p. 73.

$$K(k)=\ln\frac{4}{k'}+\frac{\ln(4/k')-1}{4}k'^2+\frac{9}{64}(\ln 4/k'-7/6)k'^4+\cdots,$$

which, upon insertion into (IV7), yields to a sufficient degree of accuracy[28]

$$\mathcal{J}_m=\frac{\pi^2}{16(6)^{\frac{1}{2}}}\left[\ln 16+\frac{1}{32}\ln\frac{16}{e^2}\right]=0.70.\quad\text{(IV8)}$$

[28] The contribution of the third term of the series is left out. This omission again minimizes the result.