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Impurity-band hopping Hall mobility revisited

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Abstract. Incorporating the passive role of the phonon reservoir (dephasing) in the time development of the electron system via modification of the generalized stochastic Liouville equation method, a theory of the impurity-band hopping Hall mobility parallel to the approach of Holstein and Friedman is constructed. Owing to the dephasing, the mobility is found to consist of two contributions. The standard one reproduces the Holstein and Friedman results while the non-standard one is found to increase with decreasing temperature at very low T for a model with positive power-law density of site energies near the band edge.

1. Introduction

The aim of the present work is to present in more detail a theory of the DC impurity-band hopping Hall mobility, with applications, which is parallel to an older approach of Holstein and Friedman (Friedman and Holstein 1963, Holstein and Friedman 1968, Friedman 1971, Holstein 1990). In our approach, one can always find a direct correspondence with the Holstein and Friedman theory with all details included. However, our approach is generalized in several respects:

(a) we are able to incorporate not only the active role of the phonon bath (which is likely to be of minor importance at low T) but also its passive role (dephasing), determining uniquely the position of energy poles with respect to the real axis; for the definition of the active (passive) role see below;

(b) having thus well defined formulae, one can show that care in handling them leads then to more than one contribution to the hopping Hall mobility; and

(c) having previously shown that the resulting hopping Hall mobility might in principle deviate from the standard temperature-insensitive form at low T (see Čápek 1991a), we are here able to discuss a more realistic case of the power-law decay of the density of uncorrelated site energies at the bottom of the impurity band.

One must say, however, that inclusion of the passive role of phonons is a non-trivial matter. For consistency, one needs to introduce the passive and active roles simultaneously and on the same footing. Such a possibility is provided by the stochastic Liouville equation model going back to Lax (1960) and, in exciton physics, to Primas (1961) and Haken and Strobl (1967). In our situation, we do not deal with excitons, but reformulation of the theory for charge carriers causes neither formal nor physical problems. Problems do, however, appear once we realize that the stochastic Liouville equation model is based on the idea of substituting the real phonon bath by an external stochastic potential field with some prescribed statistical properties. This means that the theory, in its original form, could only apply at very high temperatures (with respect to the band disorder and

the impurity band width at least). As rather the opposite situation is interesting for the impurity-band conduction problem, we avoid the standard stochastic Liouville equation model working with the generalized stochastic Liouville equation model as introduced by e.g., Čápek (1985) or Čápek and Szócs (1985). Since, in the latter theory, the phonon bath is treated consistently, the proper difference between, e.g., up and down phonon-assisted hopping rates (corresponding to the detailed balance condition) between localized states appears at any finite temperature.

On the other hand, this theory must be reformulated in order to keep the same form of reasoning as Holstein and Friedman. In particular, the latter theory starts from the Kubo theory of linear response (Kubo 1957). To do the same in our approach, we have to reformulate the generalized stochastic Liouville equation model still further to yield an approximate form of the time dependent Heisenberg operators for application in correlation functions entering the Kubo formula for the conductivity. This is briefly done in the next section. Section 3 is then devoted to the DC conductivity formula derived from the present approach. The rest of the paper is devoted to a discussion of the temperature dependence of the conductivity for the above model with the power law decay of the density of local energies at the band edge.

Before starting our reasoning, we should, however, mention also another type of impurity-band hopping Hall conduction theory which is based on the lowest-order Markovian kinetic equation theory in the local basis (rate-equation method) (Böttger and Bryksin 1976a, b, 1977a-c). There are, on the other hand, significant objections to such a kinetic theory, in particular:

- (1) the necessity of performing unjustified expansions before performing the DC limit;
- (2) the lack of correspondence with rigorous kinetic approaches, with cancellation of the electric-field-independent (Čápek 1991b) (or appearance of the electric-field-dependent (Chen and Su 1989)) transfer rates even in the electric-field-linearized theory; and
- (3) the disturbance of some exact identities (necessary to preserve correspondence with the Kubo linear-response theory) owing to the finite order expansion involved (Čápek 1988a, 1990, 1991b).

In order to illustrate why this type of theory is in fact completely uncertain regarding the validity of the results obtained, let us mention that for, e.g., the disorder to be sufficiently strong, the Anderson localization of eigenstates of H_{el} appears. Then, in the representation of these localized eigenstates, the site off-diagonal elements of H_{el} disappear and instead, site off-diagonal terms in H_{el-ph} appear. So, the Hamiltonian is the same as in standard treatments of phonon-assisted hopping. Let us recall then that the derivation of the rate equations leading to the random resistance network (governed by classical Kirchhoff laws) as in the above treatment is in fact (up to technical details) the same as that performed by Miller and Abrahams (1960). This derivation (and consequently, all the random resistance network analogy) is fully correct in the lowest-order (in the nearest-neighbour overlap parameter) theories in which expansion is performed before taking, e.g., the DC limit. On the other hand, it completely breaks down if one goes properly to infinite-order (as necessary for any finite although possibly weak coupling) theory in the above parameter. This was unequivocally proved for the first time by Čápek (1988b) who found a full cancellation of terms responsible for the appearance of the random resistance network. In order to understand the physical reasons for failure of the usual kinetic-equation approach, one should realize that in general, one cannot in fact expand well (for purposes of DC quantities) to finite order in powers of *any* (possibly even small but finite) parameter before extracting the relevant result from, e.g., *exact* kinetic equations and performing the DC limit explicitly. The point is that in the

opposite case (when expanding, e.g., in time differential equations, trying to solve them and to take the DC limit of the solution afterwards), one in fact assumes that the finite (coupling or overlap) parameter is (in a sense) small as compared to the frequency which makes the area of validity of the result shrink to zero in the DC limit. Thus, this is the incorrect order of limiting processes connected with finite-order expansion in the derivation of the approximate rate equations, which mathematically as well as physically fully disqualifies the standard rate-equation treatment in the DC limit as used by Böttger and Bryksin (1976a, b, 1977a–c). More explicitly, after performing the DC limit, the interval of allowed values of overlap integrals in the latter treatment degenerates to zero. For correction terms (formally of higher order in the expansion parameter and omitted in the rate-equation treatments although diverging in the DC limit) in the representation of eigenstates of H_{el} localized in the Anderson sense see the article by Čápek (1988a).

At this point, one should realize that the above theories do not even agree well with those of Holstein and Friedman (Friedman and Holstein 1963, Holstein and Friedman 1968, Friedman 1971, Holstein 1990). The point is that the rate-equation theories predict that the Hall mobility should, e.g., become zero in the low-temperature limit (compare equations (4.9) and (4.11) of Böttger and Bryksin (1977c)). As usually temperature-insensitive but sometimes even increasing Hall mobility with decreasing temperature is experimentally observed (see below), we shall not dwell on the rate-equation theories any longer here.

2. Principles

We start from the Hamiltonian

$$H^{tot} = H_{el} + H_{ph} + H_{el-ph} \tag{2.1a}$$

$$H_{el} = \sum_m \varepsilon_m a_m^\dagger a_m + \sum_{m \neq n} J_{mn} a_m^\dagger a_n \tag{2.1b}$$

$$H_{ph} = \sum_k \hbar \omega_k b_k^\dagger b_k \tag{2.1c}$$

$$H_{el-ph} = \frac{1}{\sqrt{N}} \sum_k \sum_{mn} g_k^{mn} \hbar \omega_k a_m^\dagger a_n (b_k + b_k^\dagger). \tag{2.1d}$$

$\varepsilon_n = \varepsilon_n(\mathbf{H})$ are random magnetic-field dependent local electron energies, $J_{mn} = J_{mn}(\mathbf{H})$ are hopping (resonance or transfer) integrals, ω_k designate harmonic phonon frequencies and g_k^{mn} are electron–phonon coupling constants. Spins are for simplicity ignored here; $a_m^\dagger = a_m^\dagger(\mathbf{H})$ and $a_m = a_m(\mathbf{H})$ are then creation and annihilation operators of electrons in a local \mathbf{H} -dependent basis. Designating the Liouville superoperators

$$L^{tot} \dots = (1/\hbar)[H^{tot}, \dots] \quad L_{el} \dots = (1/\hbar)[H_{el}, \dots] \tag{2.2}$$

one can turn, as shown by (Čápek 1985), the Liouville equation

$$i(\partial/\partial t)\rho(t) = L^{tot}\rho(t) \tag{2.3}$$

for the electron–phonon density matrix $\rho(t)$ (using the standard projection technique and the Born–Markov approximation or similarly as in the article by Čápek and Szöcs (1985)) to

$$i\frac{\partial}{\partial t}\rho_{mn}^{el}(t) = [L\rho^{el}(t)]_{mn} = \sum_{pq} L_{mnpq}\rho_{pq}^{el}(t) = [L_{el}\rho^{el}(t)]_{mn} + i\sum_{pq} \Lambda_{mnpq}\rho_{mn}^{el}(t). \tag{2.4}$$

Here $\rho_{mn}^{\text{el}}(t)$ are matrix elements of the electron density matrix

$$\rho^{\text{el}}(t) = \text{Tr}_{\text{ph}} \rho(t) \quad (2.5)$$

in the localized basis. Coefficients Λ_{mnpq} (turning into

$$\Lambda_{mnpq} = \delta_{mn}\delta_{pq}2\left(\gamma_{mp} - \delta_{mp}\sum_r \gamma_{rm}\right) - (1 - \delta_{mn})\delta_{mp}\delta_{nq}(\Gamma_m + \Gamma_n) + 2(1 - \delta_{mn})\delta_{mq}\delta_{np}\bar{\gamma}_{mn} \quad (2.6)$$

where

$$\Gamma_m = \sum_r \gamma_{rm}$$

in the Haken–Strobl (1967) parametrization) describe the influence of the phonons, L then designates the effective Liouville superoperator of the generalized stochastic Liouville equation model. One should mention that, in contradistinction to the original Stochastic Liouville Equation model (Reineker 1982), $\bar{\gamma}$ may be complex and the symmetry relation $\gamma_{mn} = \gamma_{nm}$ may become disturbed (in accordance with the detailed balance condition) provided that the sites (local impurity centres) m and n are not equal.

At this point, one should mention that the Haken–Strobl γ_{mn} parameters enter (2.6) (and, correspondingly, the stochastic Liouville equation (2.4)) in two different roles. The first one is connected with the first term in (2.6). Introducing this term into (2.4) one reveals that they give rise to the usual rate term (for the diagonal elements of the density matrix, i.e. probabilities) known from the Pauli master equations. Thus, here, these γ_{mn} coefficients determine the active role of phonons giving rise to the phonon-assisted (i.e. inelastic) hopping rates ($2\gamma_{mn}$ for the transfer $n \rightarrow m$) for the electron in question. In the definition of these coefficients (see, e.g., Čápek 1985), in the lowest order in the resonance J_{mn} integrals at least, δ functions in energy are revealed, confirming the inelastic character of these processes. On the other hand, one should realize that, *in contrast with all usual* and in this respect less advanced theories of the impurity band hopping Hall mobility, our method (in the same way as the original stochastic Liouville equation method itself) also includes the passive role of phonons. This is connected with the second term in (2.6) where our γ_{mn} coefficients enter via Γ_r coefficients. In (2.4), one can see that these coefficients cause the transversal relaxation of the site off-diagonal elements of the single-electron density matrix ρ^{el} . Such elements have of course no direct connection with the electron transport in space, which is determined by the diagonal elements, i.e. site occupation probabilities. On the other hand, owing to the first term on the right-hand side of (2.4), the diagonal and off-diagonal elements are intermixed. In particular, via this term, the passive (in the sense of the above definition) role of the phonons enters transport problems in space. This observation is, in our opinion, the most important point in our approach from the point of view of the physics of the processes involved. Technically, ignoring the above passive role leads to uncertainties in the definitions of energy denominators (for the purposes of defining their reciprocals entering transport formulae) whenever the latter become zero; in our theory (because of proper inclusion of the passive role of the phonons, i.e. dephasing), however, all the energy denominators of the type $\varepsilon_n - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_n)$ (see below from (2.11)) become non-zero with non-zero Γ_r values, i.e. their reciprocals are well defined.

Equations (2.4) determine the time dependence of ρ^{el} . Instead, in our situation, we need the (approximate) time dependence of the Heisenberg electron operators $A(t)$ determined in such a way that

$$\text{Tr}_{\text{el}}[\rho^{\text{el}}(t)A] = \text{Tr}_{\text{el}}\left\{\left[\exp(-iLt)\rho^{\text{el}}(0)\right]A\right\} = \text{Tr}_{\text{el}}\left[\rho^{\text{el}}(0)\exp(iL^\dagger t)A\right] \equiv \text{Tr}_{\text{el}}[\rho^{\text{el}}(0)A(t)]. \quad (2.7)$$

Here L^\dagger means the Hermitian conjugate superoperator to L with respect to the Hilbert-Schmidt scalar product of operators

$$(A, B) = \text{Tr}_{\text{el}}(A^\dagger B). \quad (2.8)$$

Thus

$$(L^\dagger)_{mnpq} = (L_{pqmn})^*. \quad (2.9)$$

In this way, one can then calculate the velocity-velocity correlation function

$$\langle v_\mu v_\nu(t) \rangle = \sum_{mnpq} \langle m|v_\mu|n \rangle \langle p|v_\nu|q \rangle \text{Tr}_{\text{el}}\left\{\rho_{\text{eq}}^{\text{el}} a_m^\dagger a_n [\exp(iL^\dagger t)(a_p^\dagger a_q)]\right\}. \quad (2.10)$$

For simplicity, we put $\tilde{\gamma}_{rs} = 0$ in what follows. The reason is that $\tilde{\gamma}_{rs}$ parameters are proportional to the second order in S (the small parameter of overlap of our localized electronic states with creation and annihilation operators $a_m^\dagger(\mathbf{H})$ and $a_m(\mathbf{H})$). Because both the off-diagonal matrix elements of velocity on the right-hand side of (2.10) are proportional to S , omission of $\tilde{\gamma}_{rs}$ cannot yield any error in the theory up to the third order in S . As we are going to construct such a theory, $\tilde{\gamma}_{rs}$ may be taken as zero. Then, to the third order in S ,

$$\int_0^{+\infty} \langle v_\mu v_\nu(t) \rangle dt = i\hbar \sum_{mn} \frac{\langle m|v_\mu|n \rangle}{\varepsilon_m - \varepsilon_n + i\hbar(\Gamma_m + \Gamma_n)} n_{\text{F}}(\varepsilon_m) [1 - n_{\text{F}}(\varepsilon_n)] \left(\langle n|v_\mu|m \rangle - \sum_p \frac{J_{mp}(\mathbf{H}) \langle p|v_\nu|m \rangle}{\varepsilon_p - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_p)} + \sum_p \frac{\langle n|v_\nu|p \rangle J_{pn}(\mathbf{H})}{\varepsilon_n - \varepsilon_p + i\hbar(\Gamma_p + \Gamma_n)} \right) + \mathcal{N}(S^4) \quad (2.11)$$

where

$$n_{\text{F}}(\varepsilon) = 1 / \{\exp[\beta(\varepsilon - \mu)] + 1\}.$$

Here, one should realize that treating the linear (in the magnetic field \mathbf{H}) Hall effect, one can omit the linear terms in the \mathbf{H} dependence of ε_r and Γ_r , which disappear after taking the summation over the electron spin orientations (formally ignored here) in the paramagnetic or diamagnetic state. Thus, the only magnetic-field dependence that has to be taken (in the linear Hall effect) into account is that of J_{rs} via the standard formula

$$J_{mn}(\mathbf{H}) = J_{mn}(0) \exp\{(ie/2\hbar c)\mathbf{H}[\mathbf{m} \times \mathbf{n}]\} \\ \mathbf{n} \equiv \langle n|\mathbf{x}|n \rangle \quad \text{etc} \quad (2.12)$$

exact to the linear order in \mathbf{H} . In (2.11), it appears also via the standard approximate prescription that

$$\langle m|v_\mu|n \rangle = \langle m|(i/\hbar)[H_{\text{el}}, x_\mu]|n \rangle \simeq (i/\hbar) J_{mn}(\mathbf{H}) (\langle n|x_\mu|n \rangle - \langle m|x_\mu|m \rangle). \quad (2.13)$$

3. The DC conductivity tensor

In order to avoid possible doubts regarding the order of the DC limit and expansion, we immediately discuss the DC situation here. The DC conductivity tensor can be expressed as ($\beta = 1/k_B T$, V being the normalizing volume)

$$\sigma_{\mu\nu} = \frac{e^2 \beta}{V} \int_0^{+\infty} \langle v_\nu v_\mu(t) \rangle dt \quad (3.1)$$

which yields, upon using (2.11) and (2.13),

$$\begin{aligned} \sigma_{\mu\nu} \simeq & \frac{e^2 \beta}{V} \operatorname{Re} \sum_{mn} \frac{(\langle m|x_\mu|m \rangle - \langle n|x_\mu|n \rangle) J_{mn}(\mathbf{H})}{\varepsilon_n - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_n)} n_F(\varepsilon_m) [1 - n_F(\varepsilon_n)] \\ & \times \left(\frac{i}{\hbar} J_{mn}(\mathbf{H}) (\langle m|x_\nu|m \rangle - \langle n|x_\nu|n \rangle) \right. \\ & + \frac{i}{\hbar} \sum_p \frac{J_{np}(\mathbf{H}) (\langle p|x_\nu|p \rangle - \langle m|x_\nu|m \rangle) J_{pm}(\mathbf{H})}{\varepsilon_p - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_p)} \\ & \left. + \frac{i}{\hbar} \sum_p \frac{(\langle p|x_\nu|p \rangle - \langle n|x_\nu|n \rangle) J_{np}(\mathbf{H}) J_{pm}(\mathbf{H})}{\varepsilon_n - \varepsilon_p + i\hbar(\Gamma_p + \Gamma_n)} \right). \end{aligned} \quad (3.2)$$

Here, one should notice the major advantage of having the passive role of phonons (dephasing) included. In the opposite case (with all $\Gamma_m = 0$), the integrand in (3.1) would not decay. One would have to introduce its damping as usual via, e.g., the finite (although infinitesimal) imaginary part of the frequency (multiplying the integrand in (3.1) by $\exp(-\delta t)$) which would immediately cause possible objections regarding the order of expansion and the DC limit. (Compare the above discussion of the rate equation theories (Böttger and Bryksin 1976a, b, 1977a-c).) Except for this difference and (consequently) the possibility of using a simpler form of the Kubo formula, our approach essentially follows that of, e.g., Holstein and Friedman (1968).

First of all, let us discuss the diagonal part of σ . It is, to the lowest non-vanishing order,

$$\begin{aligned} \sigma_{\mu\mu} \simeq & \frac{\pi e^2 \beta}{V} \sum_{mn} |J_{mn}(\mathbf{H})|^2 |\langle m|x_\mu|m \rangle - \langle n|x_\mu|n \rangle|^2 \\ & \times \frac{1}{\pi} \frac{\Gamma_m + \Gamma_n}{(\varepsilon_m - \varepsilon_n)^2 + \hbar^2(\Gamma_m + \Gamma_n)^2} n_F(\varepsilon_m) [1 - n_F(\varepsilon_n)] \\ & \simeq \frac{\pi e^2}{V} \sum_{mn} |J_{mn}|^2 |\langle m|x_\mu|m \rangle - \langle n|x_\mu|n \rangle|^2 \delta(\varepsilon_n - \varepsilon_m) \left(-\frac{\partial n_F(\varepsilon_m)}{\partial \varepsilon_m} \right) \equiv \sigma. \end{aligned} \quad (3.3)$$

Here, we have used the fact that $\Gamma_m + \Gamma_n$ is typically extremely small as compared to, e.g., typical widths of the impurity bands. So, in fact, a (e.g.) temperature dependence of Γ_m has practically no impact on the temperature dependence of $\sigma_{\mu\mu}$. This corresponds to the usual opinion that the phonon-assisted transfer rates $2\gamma_{mn}$, $n \rightarrow m$ entering Γ_n (see (2.6)) do not practically influence the result for the conductivity. Thus, because of (2.12), the usual formula for the (zero-magnetic-field) drift mobility $\mu \sim \beta$ resulting from (3.3) remains valid in our approach.

Let us now assume that the external magnetic field is directed parallel to the z axis (i.e. $\mathbf{H} = (0, 0, H)$). Then one can easily verify using (2.12) that the asymmetric part of the xy conductivity component

$$\begin{aligned} \sigma_{xy}^{(a)} &\equiv \frac{1}{2}(\sigma_{xy} - \sigma_{yx}) = -\frac{e^2\beta}{2\hbar V} \text{Im} \sum_{mnp} \frac{J_{mn}(\mathbf{H})J_{np}(\mathbf{H})J_{pm}(\mathbf{H})}{\varepsilon_n - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_n)} n_F(\varepsilon_m)[1 - n_F(\varepsilon_n)] \\ &\quad \times \left\{ \frac{X_{mn}Y_{pm} - Y_{mn}X_{pm}}{\varepsilon_p - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_p)} + \frac{X_{mn}Y_{pn} - Y_{mn}X_{pn}}{\varepsilon_n - \varepsilon_p + i\hbar(\Gamma_p + \Gamma_n)} \right\} \\ &= -\frac{\beta e^3 H}{\hbar^2 c V} \sum_{mnp} \left(A_{mnp}^{(z)} \right)^2 J_{mn}(0)J_{np}(0)J_{pm}(0) n_F(\varepsilon_m)[1 - n_F(\varepsilon_n)] \\ &\quad \times \text{Re} \left[\frac{1}{\varepsilon_n - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_n)} \left(\frac{1}{\varepsilon_p - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_p)} \right. \right. \\ &\quad \left. \left. + \frac{1}{\varepsilon_n - \varepsilon_p + i\hbar(\Gamma_p + \Gamma_n)} \right) \right] + \mathcal{O}(H^3) \end{aligned} \quad (3.4)$$

where

$$X_{pm} = p_x - m_x \equiv \langle p|x|p \rangle - \langle m|x|m \rangle \quad Y_{pm} = p_y - m_y \equiv \langle p|y|p \rangle - \langle m|y|m \rangle \quad \text{etc,}$$

and $A_{mnp}^{(z)}$ is the z component of the (vector) area of the triangle subtended by sites p , n and m .

Now, one can easily check that (3.4) turns (except for a numerical factor $\simeq 1$) into equation (3.35) of Holstein and Friedman (1968) provided that in two terms on the right-hand side of (3.4), one takes e.g.

$$\begin{aligned} \text{Re} \left[\left\{ 1/[\varepsilon_n - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_n)] \right\} [\varepsilon_p - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_p)] \right] \\ \simeq -\text{Im} \left\{ 1/[\varepsilon_n - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_n)] \right\} \text{Im} \left\{ 1/[\varepsilon_p - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_p)] \right\} \end{aligned} \quad (3.5)$$

and that, as mentioned above, typical values of $\hbar\Gamma$ are much less than those of the typical impurity band widths. Using the latter fact, one can also *formally* derive equation (3.35) of Holstein and Friedman (1968) provided that one approximates

$$\begin{aligned} \text{Re} \left[\left\{ 1/[\varepsilon_n - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_n)] \right\} \left\{ 1/[\varepsilon_p - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_p)] + 1/[\varepsilon_n - \varepsilon_p + i\hbar(\Gamma_p + \Gamma_n)] \right\} \right] \\ \simeq P \left[1/(\varepsilon_n - \varepsilon_m) \right] P \frac{\varepsilon_n - \varepsilon_m}{(\varepsilon_p - \varepsilon_m)(\varepsilon_n - \varepsilon_p)} \simeq P(\varepsilon_p - \varepsilon_m)(\varepsilon_n - \varepsilon_p). \end{aligned} \quad (3.6)$$

The point is that (for uncorrelated levels and constant density of site energies everywhere on the energy axis) one then encounters the integral

$$P \int_{-\infty}^{+\infty} \frac{1}{(\varepsilon_p - \varepsilon_m)(\varepsilon_n - \varepsilon_p)} d\varepsilon_p = -\pi^2 \delta(\varepsilon_m - \varepsilon_n). \quad (3.7)$$

This is the same result as that one of the integration of the right-hand side of (3.5)

$$\begin{aligned} - \int d\varepsilon_p \text{Im} \frac{1}{\varepsilon_n - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_n)} \text{Im} \frac{1}{\varepsilon_p - \varepsilon_m + i\hbar(\Gamma_m + \Gamma_p)} \\ \simeq -\pi^2 \int d\varepsilon_p \delta(\varepsilon_n - \varepsilon_m) \delta(\varepsilon_p - \varepsilon_m) = -\pi^2 \delta(\varepsilon_m - \varepsilon_n). \end{aligned} \quad (3.8)$$

This type of reasoning, although convincing at first sight, is unfortunately not sufficiently justified. The arguments leading to (3.6) are shown to be mathematically not fully rigorous (not only for non-constant density of site energies in real materials) by Čápek (1991a) while (3.5) is trivially seen to be incorrect since

$$\operatorname{Re}(AB) = \operatorname{Re} A \operatorname{Re} B - \operatorname{Im} A \operatorname{Im} B. \quad (3.9)$$

Thus, from (3.4), we obtain in fact

$$\sigma_{xy}^{(a)} = \sigma_{xy}^{(a1)} + \sigma_{xy}^{(a2)} \quad (3.10a)$$

$$\left. \begin{array}{l} \sigma_{xy}^{(a1)} \\ \sigma_{xy}^{(a2)} \end{array} \right\} = \frac{2\pi^2 \beta e^3 H}{\hbar c} \int d^3 r_n \int d^3 r_p \int \rho(\varepsilon_m) d\varepsilon_m \int \rho(\varepsilon_n) d\varepsilon_n \int \rho(\varepsilon_p) d\varepsilon_p \\ \times (A_{mnp}^{(Z)})^2 J_{mn}(0) J_{np}(0) J_{pm}(0) \exp[-\beta(\varepsilon_m - \mu)] \\ \times \begin{cases} \delta(\varepsilon_n - \varepsilon_m) \delta(\varepsilon_p - \varepsilon_m) \\ [1/2\pi^2(\varepsilon_n - \varepsilon_m)] \{ [P[1/(\varepsilon_p - \varepsilon_m)]] - P[1/(\varepsilon_p - \varepsilon_n)] \}. \end{cases} \quad (3.10b)$$

Here, we have assumed for simplicity that the site energies ε_r are random (without mutual correlations), that there is no correlation between ε_r and position in space and, finally, that the charge carriers (electrons) are non-degenerate. One might call $\sigma^{(a1)}$ and $\sigma^{(a2)}$ the standard and non-standard contributions, respectively, having in mind their structure although (as seen above) the spirit of deriving the standard result by Holstein and Friedman rather corresponds to that of $\sigma^{(a2)}$. One should yet mention that (as implicitly always assumed) the Γ_r parameters describing the influence of phonons are (as far as their magnitude is concerned) really negligible and may be (as already used in (3.10)) taken as infinitesimal quantities. However, keeping them finite (although extremely small) so far has enabled us to reveal that $\sigma_{xy}^{(a)}$, and therefore also the Hall mobility, contains surprisingly two different contributions.

At this point, an argument is worth mentioning regarding possible objections that the non-standard contribution might be, owing to its strange form containing no δ functions ensuring the site-energy coincidence, possibly due to a subtle, perhaps calculational error. We should like to turn the reader's attention to the fact that not the standard but the non-standard contribution (in our sense) was in fact derived in, e.g., the classical Holstein and Friedman (1968) paper. One can check it, ignoring in, e.g., (3.2) all the Γ_r coefficients in the energy denominators and proceeding then as usual. (For a formal correspondence, one would, however, have to introduce, as in standard theories, a non-zero frequency $\Omega = \omega + i\delta$, to neglect all Γ and then to take the DC limit $\Omega \rightarrow 0$. To this order of limits which is in fact physically incorrect, we shall return below.) The fact that this non-standard term is then given, in standard papers, the usual form with the product of two δ functions in energy, is then solely due to arguments of the type of (3.7) in the last step of formal manipulations which is (at least but not only (see above) for reasons of generally non-constant density of states) simply omitted here. So, one can easily argue against the above objections about possible error in our treatment, realizing that omitting (as we do) the last independent step in formal manipulations should not cause any change in experimental predictions. In any case, if this *does* yield different conclusions (as we are going to illustrate below), the difference cannot be ascribed to our reasoning but rather to an insufficient accuracy of the crucial step in standard theories overlooked by others. In order to see the difference, our treatment in the next section then regards specially the relevant $\sigma_{xy}^{(a2)}$ contribution.

At this point, one should be more explicit in speaking about arguments of the type of (3.7) in standard papers. In, e.g., Holstein and Friedman's (1968) paper, one certainly does not invoke such simple arguments, at least at first sight. One should, however, mention that, e.g., formula (3.28) of Holstein and Friedman (1968) makes in fact the same assumptions. This formula is certainly generally incorrect and can be (as convincing arguments by Holstein and Friedman (1968) show) correct only in the context of their formulae characterized by the '0/0' uncertainty necessary to disentangle the DC limit. Our result, because of the inclusion of dephasing, contains no such uncertainty and has already been taken directly at zero frequency. Because of the dephasing and the correct order (in contrast to that inherent to standard treatments) of limits $\Omega \rightarrow 0$ and only then $\Gamma \rightarrow 0$, it certainly incorporates contributions not seen in, e.g., the Holstein and Friedman (1968) work. (The reader is referred to such terms as $\Gamma^2/(\Gamma^2 + \Omega^2)$, which clearly disappear in the standard limit $\Gamma \rightarrow 0$ and then $\Omega \rightarrow 0$ but certainly do not do so in our, the only physically acceptable, limit $\Omega \rightarrow 0$ and only then, if at all, $\Gamma \rightarrow 0$.) Even purely formal arguments show that the standard approach is correct only to the third order in J while our approach, owing to an implicit J dependence of Γ values (compare Čápek and Szöcs (1985)), is formally summed up to infinity beyond this third order. Thus, in our more general situation, we certainly must refrain from arguments such as (3.28) of Holstein and Friedman (1968). That is why, in our more general situation, standard arguments about the presence of only triple-energy-coincidence contributions fail and why, therefore, additional contributions appear.

In this connection, one can also argue that no additional contributions might be expected when including, as in this paper, the dephasing owing to the passive role of phonons, as the imaginary part of the complex frequency $\Omega = \omega + i\delta$ (i.e. δ) also plays, in standard treatments, this role. The careful reader can easily find that this argument is certainly incorrect because keeping δ finite, all arguments leading to, e.g., formula (3.28) of Holstein and Friedman (1968) (for which the limit $\Omega \rightarrow 0$ is crucial) fail.

So repeating why, in our belief, one should at least carefully scrutinize (if not directly refrain from) all the standard treatments, we come to the conclusion that this is owing to the unphysical regime ($|\Omega| \gg \Gamma \rightarrow 0$) inherent in standard theories. In reality and our in approach, we have $\Gamma \gg |\Omega| \rightarrow 0$ and only after that (if at all), can we also take contingently $\Gamma \rightarrow 0$.

4. Consequences for experiment

In our previous article (Čápek 1991a), we have argued that $\sigma_{xy}^{(a1)}$ in (3.10b) reproduces the standard result of a temperature-independent Hall mobility

$$\mu_H = (c/\sigma) \left(d\sigma_{xy}^{(a1)} / dH \right) |_{H=0} \tag{4.1}$$

while $\sigma_{xy}^{(a2)}$ is mainly responsible for the final form

$$\mu_H \simeq \text{constant} \times \{ [\ln(2\beta\Delta)]^2 - 2C \ln(2\beta\Delta) + C^2 + \frac{29}{6}\pi^2 \} \tag{4.2}$$

(C being the Euler constant) *provided* that we assume a step-like density of states

$$\rho(\varepsilon) = \begin{cases} 0 & \varepsilon \notin (-\Delta, \Delta) \\ \rho_0 = \text{constant} & \varepsilon \in (-\Delta, \Delta) \end{cases} \tag{4.3}$$

and that we have very low temperatures ($\beta\Delta \gg 1$). (For $\beta\Delta \ll 1$ we again obtain $\mu_H = \text{constant}$.) This is rather surprising because (as already mentioned above) this was this non-standard contribution $\sigma_{xy}^{(a2)}$ which was derived by, e.g., Holstein and Friedman (1968). The reader should, however, again realize that we have, in $\sigma_{xy}^{(a2)}$, done nothing but (for physical as well as formal reasons as also mentioned above) refrained from the last stage of formal manipulations in the above paper. The result is encouraging in the sense that (4.2) yields (at least for the model density of states (4.3)) increasing values of the Hall mobility with decreasing temperature. This not only contradicts the standard result of the temperature-insensitive μ_H (such a contribution is in our case provided by the standard term $\sigma_{xy}^{(a1)}$) but is also incompatible with predictions of the rate-equation treatments (according to which μ_H always decreases with decreasing temperature) mentioned above. The question then immediately appears of whether this behaviour is an artefact of (4.3). Experimentally, increasing values of μ_H are sometimes observed (Höschl *et al* 1988). In any case, attempts to fit (4.2) to these experimental data on narrow-gap CdHgTe were not fully successful for realistically narrow impurity band widths. Other model densities of states should therefore be investigated.

One should turn the reader's attention to the fact that (3.10b) is a non-trivial nine-dimensional integral. We were therefore happy to find another form of the model density of states, which is analytically treatable and for which the increase of μ_H with decreasing temperature is determined by another quantity (different from the impurity band width). This is the case of the density of states

$$\rho(\varepsilon) = \begin{cases} 0 & \varepsilon < 0 \\ \sim \varepsilon^\lambda & \varepsilon \rightarrow 0+. \end{cases} \quad (4.4)$$

First, let us mention that (3.3) and (3.10b) yield

$$\sigma \simeq \exp(\beta\mu) \quad \sigma_{xy}^{(a1)} \simeq \exp(\beta\mu) \quad (4.5)$$

i.e. (see (4.1) and (3.10b))

$$\mu_H = \mu_H^{(1)} + \mu_H^{(2)} \quad (4.6)$$

with

$$\mu_H^{(1)} = \text{constant}. \quad (4.7)$$

So, we will pay attention to just the non-standard term in (3.10b).

One should mention here one striking feature of $\sigma_{xy}^{(a2)}$ in (3.10b): the value of $\sigma_{xy}^{(a2)}$ depends not only on the density $\rho(\varepsilon_r)$ of ε_r or that of the transfer integrals $J_{rs}(0)$ in the vicinity of the bottom of the band when μ lies below it for the carriers to be non-degenerate (or in the vicinity of μ in the opposite case) as it is usual in standard theories and as applies also for $\sigma_{xy}^{(a1)}$. $\sigma_{xy}^{(a2)}$ depends also on relatively distant (as compared to $k_B T$) areas on the energy axis. Although this is (in kinetic theories) rather an unusual case (for another such case see, e.g., Čápek 1989), this phenomenon may still be well interpreted as being, e.g., owing to the usual quantum-mechanical perturbational contributions of distant zeroth-order (in J_{rs}) states to perturbed electron eigenstates in the vicinity of the bottom of the band (or μ as above). To support this interpretation, it is worth mentioning that $\rho(\varepsilon_r)$ in (3.10b) does not in fact describe the genuine density of states but only the density of ε_r (i.e. the

density of states for the zero-hopping case $J_{rs} = 0$). So, we shall not dwell on this point any longer.

Assume now that $\rho(\varepsilon)$ is now given as in (4.4). Then $\varepsilon = 0$ is the bottom of the band and (3.10b) yields

$$\begin{aligned} \sigma_{xy}^{(a2)} \simeq & \text{constant} \times \beta H \int d\varepsilon_m \exp[-\beta(\varepsilon_m - \mu)] \rho(\varepsilon_m) \int d\varepsilon_n \frac{\rho(\varepsilon_n)}{\varepsilon_n - \varepsilon_m} \int d\varepsilon_p \rho(\varepsilon_p) \\ & \times \left[P\left(\frac{1}{\varepsilon_p - \varepsilon_m}\right) - P\left(\frac{1}{\varepsilon_p - \varepsilon_n}\right) \right]. \end{aligned} \quad (4.8)$$

From (4.8), one can see that just ε_m in the vicinity of $\varepsilon = 0$ ($0 < \varepsilon_m \lesssim k_B T$) play a role when $T \rightarrow 0$. Further, from (4.4), one can see that

$$\begin{aligned} & \int d\varepsilon_p \rho(\varepsilon_p) \left[P\left(\frac{1}{\varepsilon_p - \varepsilon_m}\right) - P\left(\frac{1}{\varepsilon_p - \varepsilon_n}\right) \right] \\ & \rightarrow \int d\varepsilon_p \rho(\varepsilon_p) \left[P\left(\frac{1}{\varepsilon_p}\right) - P\left(\frac{1}{\varepsilon_p - \varepsilon_n}\right) \right] \end{aligned} \quad (4.9)$$

(when $\varepsilon_m \rightarrow 0$) where the right-hand side of (4.9) is finite for $\lambda > 0$ as we shall always assume henceforth. Thus, at $T \rightarrow 0$,

$$\begin{aligned} \sigma_{xy}^{(a2)} \simeq & \text{constant} \times \beta H \int_0^{+\infty} d\varepsilon_m (\varepsilon_m)^\lambda \exp[-\beta(\varepsilon_m - \mu)] \\ & = \text{constant} \times H \exp(\beta\mu) (k_B T)^\lambda. \end{aligned} \quad (4.10)$$

Here, we have used the fact that the right-hand side of (4.9) is independent of ε_m so that the integral $\int d\varepsilon_n \dots$ in (4.8) simply reduces to a T -independent constant.

Now, let us return to the (diagonal part of the) DC conductivity σ . For our form of $\rho(\varepsilon)$ in (4.4), (3.3) yields

$$\sigma \simeq \text{constant} \times \exp(\beta\mu) (k_B T)^{2\lambda}. \quad (4.11)$$

Thus,

$$\mu_H \simeq (k_B T)^{-\lambda}. \quad (4.12)$$

So, according to this theory and for the model density of states (4.4), one should expect (negative) power-law increase of the impurity-band hopping Hall mobility near the bottom of the band at very low temperatures. The power (exponent) in (4.12) is, up to the sign, given by that in the density of states in (4.4). Although it might in principle be possible to determine the power from experiment, its exact value is currently very difficult to obtain because of noisy low temperature experimental data as well as the necessity to extend measurements to extremely low temperatures. As an illustration, analysis of experimental data on CdHgTe reported by Höschl *et al* (1988) shows an evident increase of μ_H with decreasing temperature above He temperature which already contradicts standard results. On the other hand, it is still impossible to decide whether these experimental data indicate divergent or regular behaviour at $T \rightarrow 0$ (Grill 1992).

The last point to be mentioned here is why in the limit $\lambda \rightarrow 0+$, the form of our prediction (4.12) does not resemble (4.2) at all. We have verified that this seeming lack of correspondence is due to the fact that the usual criteria for converting the order of limit and integration are not (in, e.g., (4.8)) fulfilled.

5. Conclusions

Theory of the impurity-band hopping Hall conductivity based on the generalized Stochastic Liouville equation model is presented, which generalizes the classical treatment by Holstein and Friedman. Meticulous inclusion of both the active and, in particular, the passive contribution of the bath to the electron transfer (phonon-assisted transfer and dephasing of the single-electron density matrix, respectively) confirms the standard Holstein and Friedman result for the impurity-band hopping Hall mobility μ_H but, in addition, it reveals another (additive) correction. The low-temperature asymptotic of the latter correction are shown to behave as $T^{-\lambda}$ for the impurity band density of states $\rho(\varepsilon) \simeq \varepsilon^\lambda$ near the lower edge of the band. This potentially increasing character of μ_H with decreasing temperature is a novel feature of the theory (not known in other approaches), which is argued to correspond to some experimental data.

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