AC phonon-assisted hopping conductivity from generalised Master equations

1990 J. Phys.: Condens. Matter 2 5345

(http://iopscience.iop.org/0953-8984/2/24/007)

J. Phys.: Condens. Matter 2 (1990) 5345–5355. Printed in the UK

AC phonon-assisted hopping conductivity from generalised Master equations

V Čápek†
International Centre for Theoretical Physics, 34100 Trieste, Italy

Received 14 August 1989, in final form 26 February 1990

Abstract. An intermediate-coupling generalised Master equation theory of AC phonon-assisted hopping conductivity is developed. Non-negligible corrections to the standard Markovian result are obtained.

1. Introduction

It is indisputable that the generalised Master equation (GME) approach to DC (or very-low-frequency) phonon-assisted hopping conductivity preserving the correct order of limits, i.e. with no expansion in powers of the electron–phonon coupling constant g before performing the DC limit $\omega + i\delta \to 0$ (Čápek 1987, 1988a–c), essentially changed our understanding of this type of transport. In particular, it became clear that local-field-induced shifts $\delta\mu_n$ of the chemical potential playing a crucial role in the lowest-order Markovian theory leading to the Kirchhoff network (Miller and Abrahams 1960) become fully cancelled by higher-order (in g) corrections to the driving term of the network equations (Čápek 1988b). Moreover, it was established that the standard lowest-order Markovian theory based on the usual rate equations

$$\frac{\partial}{\partial t} f_m(t) = \sum_{n(\neq m)} \{W_{mn} f_n(t)[1 - f_m(t)] - W_{nm} f_m(t)[1 - f_n(t)]\} \tag{1}$$

may be reconciled with the exact GME just when an incorrect order of limits (i.e. expansion in powers of g before taking the DC limit) is used; this is so because the Markovian lowest-order theory results from GME by neglecting terms $\sim g^2/(\omega + i\delta)$ (Čápek 1988c). It is striking, however, that the DC phonon-assisted hopping conductivity results from GME (Čápek 1987, 1988a–c) in exactly the same explicit form as from the roughly approximate theory of Kasuya and Koide (1958) based on an unjustified neglect of $\delta\mu_n$ in the lowest-order Markovian approach based on (1) (i.e. on incorrect neglect of terms $\sim g^2/(\omega + i\delta)$ in this type of already approximate formulation of the problem; see Manucharyants and Zvyagin (1974)). This coincidence is, however, not fully fortuitous (Čápek 1988c).

† Present and permanent address: Institute of Physics of Charles University, Ke Karlovu 5, 121 16 Prague, Czechoslovakia.

0953-8984/90/245345 + 11 $03.50

Until now, no attention has been, on the other hand, devoted to the AC phonon-assisted hopping conductivity problem starting from GME. This has been so mainly owing to technical complications connected with the fact that, for $\omega + i\delta \neq 0$, $g^2/(\omega + i\delta)$ is finite but may be much less than unity as well as much greater than unity. (Moreover, this ratio usually appears in combinations with different types of overlap integral which might be more or less arbitrary for different pairs of states.) This work is our first attempt to fill this gap.

2. General theory

Let us start by specifying our Hamiltonian in the standard form as

$$H = H_e + H_{ph} + H_{e\text{-}ph} = H_0 + H_{e\text{-}ph} = \sum_r \sum_{s=\pm\frac{1}{2}} \varepsilon_r a_{rs}^+ a_{rs} + \sum_K \hbar\omega_K b_K^+ b_K$$

$$+ \frac{g}{\sqrt{2\Omega}} \sum_{pr} \sum_{s=\pm\frac{1}{2}} \sum_K U_{pr}^K a_{ps}^+ a_{rs} (b_K + b_K^+). \tag{2}$$

Here s, ε_r, ω_K, Ω and $U_{pr}^K = \langle p|U^K|r\rangle$ are the spin index, the single-electron energy for a particle in a localised eigenstate ($|r\rangle$) of H_e, the harmonic phonon frequency, the normalising volume and the electron–phonon interaction matrix element, respectively. (This Hamiltonian is clearly approximate; the possible role of some important terms and mechanisms omitted in (2) but taking place in reality as well as that of approximations used here and below will be briefly mentioned in section 6. One should also note that, in fact, our reasoning in this section is rigorous as we start using (2) and approximate treatments only in section 3.) With the applied external field

$$\mathscr{E}(t) = \int \frac{d\omega}{2\pi} \mathscr{E}^{\omega+i\delta} \exp[-i(\omega + i\delta)t] \tag{3a}$$

$$\mathscr{E}(t) \to 0 \qquad t \to -\infty \tag{3b}$$

and designating the electronic dipole momentum as

$$d = e \sum_r \sum_{s=\pm\frac{1}{2}} x_r a_{rs}^+ a_{rs} \tag{4}$$

we can linearise the Liouville equation with respect to $\mathscr{E}$ as

$$i(\partial/\partial t)[\delta\rho(t)] = (1/\hbar)[H, \delta\rho(t)] - (1/\hbar)\mathscr{E}(t)[d, \rho_{eq}] = L\,\delta\rho(t) - (1/\hbar)\mathscr{E}(t)[d, \rho_{eq}]. \tag{5}$$

Here

$$\rho_{eq} = \exp(-\beta H)/\mathrm{Tr}[\exp(-\beta H)] \tag{6}$$

and

$$\delta\rho(t) = \rho(t) - \rho_{eq} = \int \frac{d\omega}{2\pi} \delta\rho^{\omega+i\delta} \exp[-i(\omega + i\delta)t] \tag{7a}$$

$$\delta\rho(t) \to 0 \qquad t \to -\infty \tag{7b}$$

with $\rho(t)$ being the electron–phonon density matrix. By a standard projection technique with a projector $D(=D^2)$, we obtain from (5)

$$\frac{\partial}{\partial t}[D\delta\rho(t)] = -\mathrm{i}DLD\delta\rho(t) - \int_{-\infty}^{t} DL\exp[-\mathrm{i}(1-D)L(t-\tau)](1-D)$$
$$\times\left\{-\frac{1}{\hbar}\mathscr{E}(\tau)[d,\rho_{\mathrm{eq}}] + LD\delta\rho(\tau)\right\}\mathrm{d}\tau + \frac{\mathrm{i}}{\hbar}\mathscr{E}(t)D[d,\rho_{\mathrm{eq}}]. \tag{8}$$

Using the retarded Fourier transformation, (8) turns out to be

$$[\![z - DLD - DL\{1/[z-(1-D)L]\}(1-D)LD]\!]D\delta\rho^z$$
$$= -(1/\hbar)\mathscr{E}^z D[d,\rho_{\mathrm{eq}}] - (1/\hbar)\mathscr{E}^z DL\{1/[z-(1-D)L]\}$$
$$\times(1-D)[d,\rho_{\mathrm{eq}}] \qquad z=\omega+\mathrm{i}\delta. \tag{9}$$

Here, for $z\neq 0$, expanding in powers of g to the lowest order, multiplying by $a_{rs}^{+}a_{rs}$ and taking the trace, one obtains the linearised form of (1) which has, however, no explicit solution (Čápek 1988c). As stressed above, however, this would mean a return to the standard treatment which becomes incorrect at small frequencies. Instead, therefore, we apply some exact algebra to (9) showing that

$$DL\{1/[z-(1-D)L]\}(1-D)[d,\rho_{\mathrm{eq}}]$$
$$= [\![1 - DL\{1/[z-(1-D)L]\}]\!]DL[1/(z-L)](1-D)[d,\rho_{\mathrm{eq}}]$$
$$= [\![1 - DL\{1/[z-(1-D)L]\}]\!]D\{-1+z[1/(z-L)]\}(1-D)[d,\rho_{\mathrm{eq}}]$$
$$= [\![z - DLD - DL\{1/[z-(1-D)L]\}(1-D)L]\!]$$
$$\times D[1/(z-L)](1-D)[d,\rho_{\mathrm{eq}}]. \tag{10}$$

Therefore, the explicit solution to the exact (linearised in $\mathscr{E}$) GME (9) exists and equals

$$D\delta\rho^z = -(1/\hbar)\mathscr{E}^z[D[1/(z-L)](1-D)$$
$$+ (1/[\![z - DLD - DL\{1/[z-(1-D)L]\}(1-D)LD]\!])D][d,\rho_{\mathrm{eq}}]$$
$$= -(1/\hbar)\mathscr{E}^z D[1/(z-L)][d,\rho_{\mathrm{eq}}]. \tag{11}$$

Here, we have used the fact that (as in for example the partitioning technique)

$$D[1/(z-L)]D = D/\{z - L - L[(1-D)/(z-L)]L\}$$
$$= (1/[\![z - DLD - DL\{1/[z-(1-D)L]\}(1-D)LD]\!])D. \tag{12}$$

Now, we specify our projection superoperator D as

$$(DA)_{l\lambda,m\mu} = \rho^R_{\lambda\mu}\delta_{lm}(\mathrm{Tr}_{\mathrm{ph}}\,A)_{lm} \tag{13}$$

where A is arbitrary, ρ^R fulfils the condition

$$\sum_{\lambda}\rho^R_{\lambda\lambda} = 1 \tag{14}$$

and the subscripts l, m (λ, μ) designate many-body electron (phonon) eigenstates of $H_{\mathrm{e}}(H_{\mathrm{ph}})$. Then

$$DLD = 0. \tag{15}$$

The term

$$1/[\![z - DL\{1/[z-(1-D)L]\}(1-D)LD]\!]$$

gives rise to terms

$$\sim 1/(z+\mathrm{i}/\tau) = -\mathrm{i}\tau/(1-\mathrm{i}\tau z)$$

in the lowest order in g in the usual kinetic theories of relaxing systems (τ is the lowest-order relaxation time). In these theories, such terms result from dividing the kinetic

equation (in the Fourier picture) by its left-hand side (compare (9)). Because, however, our kinetic equation (GME) (9) (in particular its right-hand side) is exact to all powers of g, such a term cancels in the exact solution (11). On the other hand, the term $\sim 1/(1 - i\tau z)$ in the solution for the AC conductivity for example has a sound physical meaning given by correspondence to experiment (see the next section). Its origin in the GME theory must be therefore looked for somewhere else than on the *left*-hand side of the exact (to all powers of g) kinetic equation (GME) (9). In section 4, we shall see that this term results from higher-order terms in expansion of the *right*-hand side of (9) or its solution (11). Here, we should just like to mention that, up to now, no real use of our Hamiltonian (2) has been made. Thus, the conclusion about the origin of the terms $\sim 1/(1 - i\tau z)$ is rigorous and model independent.

3. The lowest order in g

In order to illustrate the importance of the above arguments about the role and origin of terms $\sim 1/(1 - i\tau z)$, let us calculate the AC conductivity from (11) keeping just the lowest-order (second-order) terms in g. In this order, from (11), we obtain

$$D\delta\rho^z = -\frac{1}{\hbar}\mathscr{E}^z D \frac{1}{z - L_0}\left(1 + \mathscr{L}\frac{1}{z - L}\right)\left[d, \frac{\exp(-\beta H)}{\mathrm{Tr}[\exp(-\beta H)]}\right]$$

$$\simeq -\frac{1}{\hbar z}\mathscr{E}^z D\mathscr{L}\frac{1}{z - L_0}\int_0^\beta \mathrm{d}\lambda$$

$$\times \exp(-\lambda H_0)[H_{\mathrm{e\text{-}ph}}, d]\exp(\lambda H_0)\rho_{\mathrm{eq}}^{(0)} \tag{16}$$

$\rho_{\mathrm{eq}}^{(0)} = \exp(-\beta H_0)/\mathrm{Tr}[\exp(-\beta H_0)]$.

Here

$$\mathscr{L}\ldots = (1/\hbar)[H_{\mathrm{e\text{-}ph}}, \ldots] \tag{17a}$$

$$L_0\ldots = (1/\hbar)[H_0, \ldots] \tag{17b}$$

and the fact has been taken into account that

$$DL_0 = L_0 D = 0 \tag{18}$$

and

$$D[d, \rho_{\mathrm{eq}}] = 0 \tag{19}$$

owing to our choice of (4) with only diagonal elements of coordinates. Thus, assuming henceforth implicitly the thermodynamic limit to be performed first, the AC conductivity

$$\sigma(\omega + i\delta) = \frac{-ie(\omega + i\delta)}{\Omega}\sum_p \sum_{s_0 = \pm\frac{1}{2}} \frac{x_p\,\mathrm{Tr}(a_{ps_0}^+ a_{ps_0} D\delta\rho^{\omega + i\delta})}{\mathscr{E}^{\omega + i\delta}}$$

$$= \frac{ie^2 g}{\hbar\Omega\sqrt{2\Omega}}\sum_{pqr}\sum_{s_0, s = \pm\frac{1}{2}}\sum_K x_p U_{rq}^K (x_q - x_r)$$

$$\times \mathrm{Tr}\left[[a_{ps_0}^+ a_{ps_0}, H_{\mathrm{e\text{-}ph}}]\left(\frac{1 - \exp[-\beta(\varepsilon_r - \varepsilon_q - \hbar\omega_K)]}{\varepsilon_r - \varepsilon_q - \hbar\omega_K}\right.\right.$$

$$\times \frac{a_{rs}^{+} a_{qs} b_K}{\hbar(\omega + i\delta) - \varepsilon_r + \varepsilon_q + \hbar\omega_K}$$
$$+ \frac{1 - \exp[-\beta(\varepsilon_r - \varepsilon_q + \hbar\omega_K)]}{\varepsilon_r - \varepsilon_q + \hbar\omega_K}$$
$$\times \frac{a_{rs}^{+} a_{qs} b_K^{+}}{\hbar(\omega + i\delta) - \varepsilon_r + \varepsilon_q - \hbar\omega_K} \Big) \rho_{eq}^{(0)} \Big] + O(q^4). \tag{20}$$

Consequently, for the real part for example

$$\text{Re } \sigma(\omega + i0+) = \frac{\pi e^2 g^2}{2\hbar\Omega^2} \sum_{qr} \sum_{K} \sum_{s=\pm\frac{1}{2}} |U_{rq}^{K}|^2 (x_q - x_r)^2 n_F(\varepsilon_q)[1 - n_F(\varepsilon_r)]$$
$$\times \{n_B(\hbar\omega_K)\delta(\hbar\omega - \varepsilon_r + \varepsilon_q + \hbar\omega_K)$$
$$+ [1 + n_B(\hbar\omega_K)]\delta(\hbar\omega - \varepsilon_r + \varepsilon_q - \hbar\omega_K)\}$$
$$\times [1 - \exp(-\beta\hbar\omega)]/\hbar\omega + O(g^4)$$
$$n_F(z) = \{\exp[\beta(z - \mu)] + 1\}^{-1} \qquad n_B(z) = [\exp(\beta z) - 1]^{-1} \tag{21}$$

with μ being the chemical potential. In order to check this result with experiment, let us assume a constant density N_F of uncorrelated electron levels with a constant localisation radius γ^{-1} of corresponding orbitals, the K modes being extended standing waves with the Debye spectrum, the temperature T being less than the Debye temperature Θ and the coupling being of the deformation potential type. Then (21) yields after lengthy but analytical integrations (compare Čápek (1976) for the DC case)

$$\text{Re } \sigma(\omega + i0+) = [E_1^2 e^2 N_F^2/\rho\hbar^8(\gamma s)^9](k_B T)^8 [\tfrac{7}{5}\pi^8 + \tfrac{35}{24}\pi^6(\beta\hbar\omega)^2$$
$$+ \tfrac{21}{320}\pi^4(\beta\hbar\omega)^4 + \tfrac{7}{128}\pi^2(\beta\hbar\omega)^6 + \tfrac{7}{3072}(\beta\hbar\omega)^8] + O(E_1^4) \tag{22}$$
$$\beta = 1/k_B T \qquad \omega \ll k_B\Theta/\hbar.$$

Here E_1 is the deformation potential (accepting the role of g here), ρ is the mass density and s is the velocity of sound. Taking the DC limit $\omega \to 0$ in (22), one easily recovers the standard GME result for the DC conductivity calculated with the proper order of limits (Čápek 1987) which corresponds well (as far as the T-dependence as well as the magnitude is concerned) to experiment (Čápek 1976). The ω-dependence of (22), however, does not correspond to experiment which seems to prefer the form

$$\text{Re } \sigma \sim \omega^s \qquad s \leqslant 1 \tag{23}$$

in a broad interval of frequencies. This disagreement may be ascribed to insufficient accuracy of (22), owing to the full omission of higher-order (in g or E_1) terms. So, we have to construct not the weak-coupling but rather an intermediate-coupling theory in the AC case in order to reconcile the theory with experiment. Here, by the intermediate theory, we mean such the kind of theory which is partially summed to infinite order in g. This itself does not yet automatically warrant, in general, its applicability in a greater area of g or in the same (as in the DC case) area for an extended interval of ω. On the other hand, when such a summation is performed systematically, one can thus include for example all the relevant single-phonon processes in all orders in g, omitting all polaron and many-phonon processes. In particular, this is the case of our approach in the next section. Thus, one can really expect that the theory may remain true even in

the AC case as long as the strength of the coupling is sufficiently weak for the many-phonon and polaron processes to be of minor importance; this may be checked by comparing for example the DC limit of (22) with experimental values of the DC conductivity.

4. Intermediate-coupling theory

We start from (11), rewriting it in the form

$$\begin{aligned} D\delta\rho^z &= -(1/\hbar)\mathscr{E}^z D\{1 + [1/(z - L)]\mathscr{L}\}[1/(z - L_0)][d, \rho_{eq}] \\ &= -(1/\hbar)\mathscr{E}^z\{D[1/(z - L)]D + D[1/(z - L)](1 - D)\} \\ &\quad \times \mathscr{L}[1/(z - L_0)][d, \rho_{eq}]. \end{aligned} \tag{24}$$

In the second equality, we have used (18) and (19). Now, in the braces in the second line on the right-hand side of (24), we neglect the second term $D[1/(z - L)](1 - D)$ as the corresponding contribution to $D\delta\rho^z$ is proportional to g^4 at least. Formally, however, because of this approximation, the result for the AC conductivity starts to depend on the choice of ρ^R in (13). In order to avoid formal introduction of polaron and many-phonon processes (which would be here beyond the scope of accuracy of the theory owing to the above approximation), we assume henceforth that

$$\rho^R = \exp(-\beta H_{ph})/\mathrm{Tr}[\exp(-\beta H_{ph})]. \tag{25}$$

Then, using (12) and (15), we obtain for the AC conductivity

$$\begin{aligned} \sigma(\omega + i\delta) \simeq \frac{i(\omega + i\delta)e}{\hbar\Omega} \sum_p \sum_{s_0 = \pm\frac{1}{2}} x_p \,\mathrm{Tr}\Big(& a^+_{ps_0} a_{ps_0} \\ & \times [\![\omega + i\delta - DL\{1/[\omega + i\delta - (1 - D)L]\}(1 - D)LD]\!]^{-1} D\mathscr{L} \frac{1}{z - L_0} \\ & \times \int_0^\beta d\lambda \exp(-\lambda H_0)[H_{e\text{-}ph}, d] \exp(\lambda H_0)\rho^{(0)}_{eq}\Big) \\ = \frac{ie^2(\omega + i\delta)g}{\hbar\Omega\sqrt{2\Omega}} \sum_{qrp} \sum_K \sum_{s, s_0 = \pm\frac{1}{2}} & U^K_{rq}(x_q - x_r) x_p \,\mathrm{Tr}\Big[a^+_{ps_0} a_{ps_0} \\ & \times [\![\omega + i\delta - DL\{1/[\omega + i\delta - (1 - D)L]\}(1 - D)LD]\!]^{-1} D\mathscr{L} \\ & \times \left(\frac{1 - \exp[-\beta(\varepsilon_r - \varepsilon_q - \hbar\omega_K)]}{\varepsilon_r - \varepsilon_q - \hbar\omega_K} \frac{a^+_{rs} a_{qs} b_K}{\omega + i\delta - \varepsilon_r/\hbar + \varepsilon_q/\hbar + \omega_K} \rho^{(0)}_{eq} \right. \\ & \left. + \frac{1 - \exp[-\beta(\varepsilon_r - \varepsilon_q + \hbar\omega_K)]}{\varepsilon_r - \varepsilon_q + \hbar\omega_K} \frac{a^+_{rs} a_{qs} b^+_K}{\omega + i\delta - \varepsilon_r/\hbar + \varepsilon_q/\hbar - \omega_K} \rho^{(0)}_{eq} \right) \Big]. \end{aligned} \tag{26}$$

Here, we may formally return to (22) when neglecting the term

$$DL\{1/[\omega + i\delta - (1 - D)L]\}(1 - D)LD = D\mathscr{L}\{1/[\omega + i\delta - (1 - D)L]\}\mathscr{L}D \sim g^2 \tag{27}$$

in the denominator in (26). Even without doing that, taking properly the DC limit $\omega + i\delta \to 0$ first, we can still reobtain a proper form of the DC conductivity (Čápek 1987):

$$\sigma_{DC} = \frac{\beta e^2}{2\Omega} \sum_{qr} \sum_{s=\pm\frac{1}{2}} W_{qr} n_F(\varepsilon_r)[1 - n_F(\varepsilon_q)](x_q - x_r)^2 + O(g^4) \tag{28}$$

$$W_{qr} = \frac{\pi g^2}{\hbar\Omega} \sum_K |U_{qr}^K|^2 \{\delta(\varepsilon_r - \varepsilon_q + \hbar\omega_K) n_B(\hbar\omega_K) + \delta(\varepsilon_r - \varepsilon_q - \hbar\omega_K)[1 + n_B(\hbar\omega_K)]\}.$$

(For the above model with deformation potential coupling, (28) coincides with the DC limit of (22).) Starting from the next approximation, however, the correspondence to the DC limit (28) is lost as this approximation is based on a reversed order of limits which is unacceptable at very low frequencies. In particular, we first approximate (27) by its lowest-order counterpart (lowest-order term in g) and then take formally the DC limit $\omega + i\delta \to 0$. Thus, from (26),

$$\begin{aligned}\sigma(\omega + i\delta) \simeq \frac{ie^2(\omega + i\delta)g}{\hbar\Omega\sqrt{2\Omega}} \sum_{qrp} \sum_K \sum_{s,s_0=\pm\frac{1}{2}} U_{rq}^K (x_q - x_r) x_p \\ \times \mathrm{Tr}\Bigg[a_{ps_0}^+ a_{ps_0} \frac{1}{\omega + i\delta - D\mathcal{L}[1/(-L_0 + i0+)]\mathcal{L}D} D\mathcal{L} \\ \times \Bigg(\frac{1 - \exp[-\beta(\varepsilon_r - \varepsilon_q - \hbar\omega_K)]}{\varepsilon_r - \varepsilon_q - \hbar\omega_K} \frac{a_{rs}^+ a_{qs} b_K}{\omega + i\delta - \varepsilon_r/\hbar + \varepsilon_q/\hbar + \omega_K} \rho_{eq}^{(0)} \\ + \frac{1 - \exp[-\beta(\varepsilon_r - \varepsilon_q + \hbar\omega_K)]}{\varepsilon_r - \varepsilon_q + \hbar\omega_K} \frac{a_{rs}^+ a_{qs} b_K^+}{\omega + i\delta - \varepsilon_r/\hbar + \varepsilon_q/\hbar - \omega_K} \rho_{eq}^{(0)} \Bigg) \Bigg].\end{aligned} \tag{29}$$

Now, one should make the term $D\mathcal{L}[1/(-L_0 + i0+)]\mathcal{L}D$ in (29) more explicit. Because of our choice of D, DA is diagonal in electron indices:

$$(DA)_{l\lambda,m\mu} \sim \delta_{lm} \tag{30}$$

for any A. Then, after some straightforward algebra, we obtain

$$\begin{aligned}\mathrm{Tr}\Bigg(a_{ps_0}^+ a_{ps_0} D\mathcal{L} \frac{1}{-L_0 + i0+} \mathcal{L}D\, DA \Bigg) \\ = -\frac{i\pi g^2}{\hbar\Omega} \sum_{nK} |U_{np}^K|^2 \{\delta(\varepsilon_p - \varepsilon_n + \hbar\omega_K) n_B(\hbar\omega_K) \\ + \delta(\varepsilon_p - \varepsilon_n - \hbar\omega_K)[1 + n_B(\hbar\omega_K)]\} \mathrm{Tr}[a_{ps_0}^+ a_{ps_0}(1 - a_{ns_0}^+ a_{ns_0}) DA] \\ = -i \sum_{n(\neq p)} W_{np} \mathrm{Tr}[a_{ps_0}^+ a_{ps_0}(1 - a_{ns_0}^+ a_{ns_0}) DA].\end{aligned} \tag{31}$$

Therefore,

$$\begin{aligned}\sigma(\omega + i\delta) \simeq \frac{ie^2(\omega + i\delta)g}{\hbar\Omega\sqrt{2\Omega}} \sum_{qrp} \sum_K \sum_{s,s_0=\pm\frac{1}{2}} U_{rq}^K (x_q - x_r) x_p \\ \times \mathrm{Tr}\Bigg\{ \Bigg[a_{ps_0}^+ a_{ps_0} \Bigg/ \Bigg(\omega + i\delta + i \sum_{n(\neq p)} W_{np} [1 - a_{ns_0}^+ a_{ns_0}] \Bigg) \Bigg] \Bigg\}\end{aligned}$$

$$\times \left[H_{\text{e-ph}}, \frac{1-\exp[-\beta(\varepsilon_r-\varepsilon_q-\hbar\omega_K)]}{\varepsilon_r-\varepsilon_q-\hbar\omega_K} \right.$$

$$\times \frac{a_{rs}^{+}a_{qs}b_K}{\hbar(\omega+\mathrm{i}\delta)-\varepsilon_r+\varepsilon_q+\hbar\omega_K}\rho_{\text{eq}}^{(0)}$$

$$\left. + \frac{1-\exp[-\beta(\varepsilon_r-\varepsilon_q+\hbar\omega_K)]}{\varepsilon_r-\varepsilon_q+\hbar\omega_K} \frac{a_{rs}^{+}a_{qs}b_K^{+}}{\hbar(\omega+\mathrm{i}\delta)-\varepsilon_r+\varepsilon_q-\hbar\omega_K}\rho_{\text{eq}}^{(0)} \right] \Bigg\}$$

$$= \frac{\mathrm{i}e^2g^2(\omega+\mathrm{i}\delta)}{4\hbar\Omega^2} \sum_{qr}\sum_{K}\sum_{s=\pm\frac{1}{2}} |U_{rq}^{K}|^2(x_q-x_r)^2 n_{\text{F}}(\varepsilon_q)[1-n_{\text{F}}(\varepsilon_r)]$$

$$\times \mathrm{Tr}\left\{ \left[1\Big/\left(\omega+\mathrm{i}\delta+\mathrm{i}W_{rq}+\mathrm{i}\sum_{n(\neq r,q)} W_{nq}(1-a_{ns}^{+}a_{ns})\right)\right.\right.$$

$$\left.\left. + 1\Big/\left(\omega+\mathrm{i}\delta+\mathrm{i}W_{qr}+\mathrm{i}\sum_{n(\neq r,q)} W_{nr}(1-a_{ns}^{+}a_{ns})\right)\right]\rho_{\text{eq}}^{(0)}\right\}$$

$$\times \left(\frac{1-\exp[-\beta(\varepsilon_r-\varepsilon_q-\hbar\omega_K)]}{\varepsilon_r-\varepsilon_q-\hbar\omega_K} \frac{n_{\text{B}}(\hbar\omega_K)}{\hbar(\omega+\mathrm{i}\delta)-\varepsilon_r+\varepsilon_q+\hbar\omega_K} \right.$$

$$\left. \times \frac{1-\exp[-\beta(\varepsilon_r-\varepsilon_q+\hbar\omega_K)]}{\varepsilon_r-\varepsilon_q+\hbar\omega_K} \frac{1+n_{\text{B}}(\hbar\omega_K)}{\hbar(\omega+\mathrm{i}\delta)-\varepsilon_r+\varepsilon_q-\hbar\omega_K} \right) \tag{32}$$

with for example

$$\mathrm{Tr}\left[1\Big/\left(\omega+\mathrm{i}\delta+\mathrm{i}W_{rq}+\mathrm{i}\sum_{n(\neq r,q)} W_{nq}(1-a_{ns}^{+}a_{ns})\right)\rho_{\text{eq}}^{(0)}\right]$$

$$= \left(1\Big/ \prod_{n(\neq r,q)} \{1+\exp[-\beta(\varepsilon_n-\mu)]\} \right)$$

$$\times \sum_{\substack{\ldots m_n\ldots=0,1 \\ (n\neq r,q)}} \left[\exp\left(-\beta \sum_{n(\neq r,q)} (\varepsilon_n-\mu)m_n \right) \right.$$

$$\left. \times \left(\omega+\mathrm{i}\delta+\mathrm{i}W_{rq}+\mathrm{i}\sum_{n(\neq r,q)} W_{nq}(1-m_n) \right)^{-1} \right]. \tag{33}$$

Factors (33) entering (32) express the influence of the third-state (fourth-state, etc) occupation fluctuation on the AC conductivity. In general, they can be easily calculated just in the limit $T \to 0$.

5. Correspondence to Markovian theory

Because the Markovian theory is not a consistently fully quantum approach (which might become important at very low temperatures), let us assume the high-temperature regime

$$k_{\text{B}}\Theta \ll k_{\text{B}}T \tag{34a}$$

$$|\varepsilon_r-\varepsilon_q| \ll k_{\text{B}}T. \tag{34b}$$

Then the exponentials in (32) may be expanded. Except for factors such as (33) multiplied by $\omega + i\delta$, we thus get almost (21) as far as

$$\hbar\omega \ll k_B T. \tag{35}$$

The result (21) is, however, almost ω independent as far as (35) applies (see (22)). This indicates that we can easily neglect $\hbar(\omega + i\delta)$ in $\hbar(\omega + i\delta) - \varepsilon_r + \varepsilon_q \pm \hbar\omega_K$ in the denominator in those terms which give rise to the hopping rates. This yields

$$\begin{aligned}\operatorname{Re}\sigma(\omega + i0+) &\simeq \frac{\beta e^2}{2\Omega}\sum_{qr}\sum_{s=\pm\frac{1}{2}} W_{rq} n_F(\varepsilon_q)[1 - n_F(\varepsilon_r)](x_q - x_r)^2 \frac{\omega^2}{\omega^2 + W_{rq}^2} \\ &+ \frac{\beta e^2 g^2}{2\hbar\Omega^2}\sum_{qr}\sum_{s=\pm\frac{1}{2}}\sum_{K} |U_{rq}^K|^2 n_F(\varepsilon_q)[1 - n_F(\varepsilon_r)](x_q - x_r)^2 \\ &\times P\left(\frac{n_B(\hbar\omega_K)}{\hbar\omega - \varepsilon_r + \varepsilon_q + \hbar\omega_K} + \frac{1 + n_B(\hbar\omega_K)}{\hbar\omega - \varepsilon_r + \varepsilon_q - \hbar\omega_K}\right)\frac{\omega W_{rq}}{\omega^2 + W_{rq}^2} \\ &\equiv \operatorname{Re}\sigma^{(1)}(\omega) + \operatorname{Re}\sigma^{(2)}(\omega).\end{aligned} \tag{36}$$

Here, we have (as usual) assumed the pair approximation (i.e. we have neglected $\Sigma_{n(\neq r,q)} W_{nq}(1 - a_{ns}^+ a_{ns})$ and $\Sigma_{n(\neq q,r)} W_{nr}(1 - a_{ns}^+ a_{ns})$ in the denominator in (32)) and assumed the high-temperature limit, i.e. $W_{qr} \simeq W_{rq}$. The summation $\Sigma_{r,q}$ in (36) is for such pairs of states which fulfil (34*b*).

The term $\operatorname{Re}\sigma^{(1)}(\omega)$ is a result of the Markovian lowest-order theory of the AC conductivity in the pair approximation (see, e.g., Efros (1981) for a short introduction) while $\operatorname{Re}\sigma^{(2)}(\omega)$ has no counterpart in this type of theory. The reason is that it is due to the Hilbert transform of the frequency-dependent hopping probability—a quantity which is unknown in the standard Markovian approach.

Starting from the Markovian theory, it has been shown many times that $\operatorname{Re}\sigma^{(1)}(\omega)$ corresponds approximately to experiment, i.e. to (23), provided that the net hopping rate may be taken as for example the exponential

$$\begin{aligned}\Gamma_{qp} = \Gamma_{pq} &= W_{pq} n_F(\varepsilon_q)[1 - n_F(\varepsilon_p)] \\ &\simeq \gamma_0 \exp[-2\gamma|x_p - x_q| - \tfrac{1}{2}\beta(|\varepsilon_p - \varepsilon_q| + |\varepsilon_p - \mu| + |\varepsilon_q - \mu|)]\end{aligned} \tag{37}$$

with a constant prefactor γ_0. So, it might be tempting to declare that $\operatorname{Re}\sigma^{(2)}(\omega)$ is just a small correction and that the GME theory confirms the standard Markovian approach to the AC conductivity in agreement with experiment. (Here, one should also realise that with (37), however, the GME result (28) contradicts experiment on the DC conductivity; compare Ambegaokar *et al* (1971).) The problem is, however, that γ_0 in (37) cannot be in fact taken as a constant as it strongly depends on $|\varepsilon_p - \varepsilon_q|$ in realistic models (Čápek 1977). Taking this into account, one gets that the GME result (28) agrees with experiment on the DC conductivity quite well. Designating therefore (28) as σ_{DC}^{GME}, we thus have using (36)

$$\operatorname{Re}\sigma^{(1)}(\omega) < \sigma_{DC}^{GME} \simeq \sigma_{DC}^{exp} < \operatorname{Re}\sigma^{exp}(\omega) \qquad \omega \neq 0 \tag{38}$$

because $\omega^2/(\omega^2 + x^2) < 1$ for $x \neq 0$. Moreover, the last inequality in (38) becomes very sharp with increasing ω. Therefore, as far as we can identify $\operatorname{Re}\sigma^{exp}(\omega)$ with (36), $\operatorname{Re}\sigma^{(2)}(\omega)$ is not a negligible correction and the GME theory thus does not fully confirm the standard Markovian theory of the AC phonon-assisted hopping conductivity. Further analysis is, however, still needed.

6. Possible effect of approximations used

One should stress that, up to equation (15), no approximations have been used. So, our result that terms $\sim 1/(1 - i\tau z)$, $z = \omega + i\delta$ do not appear in the rigorous theory as a result of dividing the kinetic equation by its left-hand side is fully general. Anyway, such terms have been, on the other hand, found as a result of approximations (expansions) on the right-hand side of the kinetic equations (GME). One should therefore discuss the possible effect of these approximations on such terms and mainly the conclusion about the existence of non-negligible corrections to the standard theory in more detail.

Some approximations are connected with the model Hamiltonian (2) used for the first time in (16). In particular, these are the omission of the particle–particle interaction term, the omission of phonon anharmonic terms and taking just the linear particle–phonon interaction Hamiltonian. Avoiding the first type of approximation leads to technical complications; for example for the Hubbard type of coupling (taking the strongest intrasite interaction into account), however, it is known that the structure of the result remains the same for all types of process connected with four possible occupancies of the initial and final particle states by particles having opposite spins to that of the hopping particle. As far as the omission of anharmonic and non-linear particle–phonon interaction terms is concerned, these are unnecessary approximations needed just to make the hopping rate formulae explicit. Finally, in (16), the fact has also been used that (4) does not include off-diagonal elements of the coordinate. These elements are, however, very small owing to small overlaps between localised states and no serious corrections are expected to result from them.

Omission of $\sim g^4$ terms in (24) and choice of (25) correspond to the aim of the paper: to construct a GME counterpart of the standard theory ignoring many-phonon and polaron effects. One cannot exclude the possibility that these effects might become important in some specific materials but, in such a case, the conclusion of the present work about non-negligible corrections to the standard AC hopping conductivity result would yet more pronounced.

In (29), we have calculated the lowest-order relaxation time term in the DC limit. This approximation becomes in principle unreliable in the DC limit as already stressed above. On the other hand, it also corresponds to the spirit of the standard approach in which this approximation is never questioned. Moreover, here, we never go to very low frequencies after equation (28). On the other hand, trying to compare (32) with the standard result, we do not exceed such a crucial frequency beyond which the frequency dependence of the hopping rates (ignored in the standard treatment) might appear. Finally, also in agreement with the (not fully consistent quantum) character of the standard Markovian approach, we assume the high-temperature limit in (34), (35). These approximations are necessary just for comparison with the standard theory on the level on which the latter theory applies.

Therefore, summarising, we see that approximations used here are not crucial for the main conclusion of this work regarding the existence of non-negligible corrections to the standard approach. Moreover, we have no reason to believe that amending the Hamiltonian or improving the approximations used might yield better physical justification of the standard theory as we do not see any physical effect omitted in (2) or other approximations used here which might be restored (or improved again) by approximations leading to the approximate lowest-order Markovian theory.

Acknowledgment

The author is grateful to Professor P N Butcher for suggesting the problem and for inspiration.

References

Ambegaokar V, Halperin B I and Langer J S 1971 *Phys. Rev.* B **4** 2612
Čápek V 1976 *Czech. J. Phys.* B **26** 1191
—— 1977 *J. Phys. Chem. Solids* **38** 623
—— 1987 *Phys. Rev.* B **36** 7442
—— 1988a *Czech. J. Phys.* B **38** 777
—— 1988b *Phys. Status Solidi* b **147** K57
—— 1988c *Phys. Rev.* B **38** 12983
Efros A L 1981 *Phil. Mag.* B **43** 829
Kasuya T and Koide S 1958 *J. Phys. Soc. Japan* **13** 1287
Manucharyants E O and Zvyagin I P 1974 *Phys. Status Solidi* b **65** 665
Miller A and Abrahams E 1960 *Phys. Rev.* **120** 745