Generalized master equations and phonon-assisted hopping

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Time-convolution generalized master equations are solved for the dc phonon-assisted hopping conductivity in disordered semiconductors, avoiding usual unphysical expansions in powers of the electron-phonon coupling before performing the dc limit. The explicit result obtained contradicts that of the lowest-order Markovian rate equations but agrees with that based on rigorous methods avoiding approximate kinetic equations. With the above-mentioned expansions, standard Markovian-rate-equation results leading contingently to the Miller-Abrahams network are reproduced.

I. INTRODUCTION

Kasuya and Koide[1] were probably the first to derive (in an approximate manner) an explicit formula for the dc phonon-assisted hopping conductivity. Starting from Markovian kinetic equations, Miller and Abrahams[2] amended their treatment by including local-field-induced changes $\delta\mu_l$ of the chemical potential at individual sites. For the standard Hamiltonian (nonrelativistic, without magnetic field)

$$H=H_e+H_{\rm ph}+H_{e\text{-ph}} , \tag{1a}$$

$$H_e=\sum_{n,\sigma}\varepsilon_n a^\dagger_{n\sigma}a_{n\sigma} , \tag{1b}$$

$$H_{\rm ph}=\sum_{\kappa}\hbar\omega_\kappa b^\dagger_\kappa b_\kappa , \tag{1c}$$

$$H_{e\text{-ph}}\equiv\mathcal{H}=\frac{g}{\sqrt{2\Omega}}\sum_{m,n}\sum_{\sigma}\sum_{\kappa}U^\kappa_{mn}a^\dagger_{m\sigma}a_{n\sigma}(b_\kappa+b^\dagger_\kappa) , \tag{1d}$$

their result for the dc conductivity reads

$$\sigma=\frac{\beta e^2}{2\Omega}\sum_{m,n}\sum_{\sigma}\Gamma_{mn}(x_m-x_n)\left[x_m-x_n-\frac{\delta\mu_m}{e\mathcal{E}}+\frac{\delta\mu_n}{e\mathcal{E}}\right] , \tag{2a}$$

with the mean equilibrium transfer rates

$$\Gamma_{mn}=\frac{\pi g^2}{\hbar\Omega}\sum_{k}|U^\kappa_{mn}|^2\{\delta(\varepsilon_n-\varepsilon_m+\hbar\omega_\kappa)n_B(\hbar\omega_\kappa)+\delta(\varepsilon_n-\varepsilon_m-\hbar\omega_\kappa)[1+n_B(\hbar\omega_\kappa)]\}n_F(\varepsilon_n)[1-n_F(\varepsilon_m)]$$
$$=W^{\rm eq}_{mn}n_F(\varepsilon_n)[1-n_F(\varepsilon_m)]=\Gamma_{nm} . \tag{2b}$$

Here $\beta=1/k_BT$, Ω, n_F (n_B), ε_m, ω_κ, U^κ_{mn}, and g are the reciprocal temperature in energy units, normalizing volume, Fermi-Dirac (Bose-Einstein) distribution, localized site energy, harmonic phonon frequency, electron-phonon interaction matrix element, and the electron-phonon coupling constant, respectively. $\mathcal{E}$ is the external field and $x_m=\langle m|\mathcal{E}\cdot\mathbf{x}/|\mathcal{E}||m\rangle$ is the coordinate of the localized single-electron eigenstate (site) $|m\rangle$ of H_e in the direction of $\mathcal{E}$. (Everywhere we assume the infinite-volume limit $\Omega\to+\infty$ before all other limiting processes mentioned below; for brevity, however, we do not designate it explicitly.) In order to introduce $\delta\mu_l$, let us write the mean number of electrons at site l out of equilibrium as

$$f_l=\frac{1}{e^{\beta(\varepsilon_l-\mu-\delta\mu_l)}+1} . \tag{3a}$$

From that, one gets the relation between the linear changes $\delta\mu_l$ in (2a) and δf_l of f_l of the form

$$\delta\mu_l=k_BT\delta f_l/n_F(\varepsilon_l)[1-n_F(\varepsilon_l)] . \tag{3b}$$

In order to determine $\delta\mu_l$, Miller and Abrahams[2] suggested using (3b) and finding δf_l from the linearized form of the intuitive low-frequency lowest-order Markovian rate equations

$$\frac{\partial}{\partial t}f_m(t)=\sum_{n(\neq m)}[W_{mn}f_n(1-f_m)-W_{nm}f_m(1-f_n)] . \tag{4}$$

Expressing then δf_l as

$$\delta f_l=-e\mathcal{E}\cdot\langle\langle a^\dagger_{l\sigma}a_{l\sigma},\mathbf{d}/e;\omega+i\delta\rangle\rangle=-e\mathcal{E}G_l(\omega+i\delta) \tag{5}$$

($\mathbf{d}$ being the electronic dipole momentum), we obtain from (4) (Refs. 2 and 3)

$$(\omega+i\delta)G_l(\omega+i\delta)=-i\beta\sum_{m(\neq l)}\Gamma_{lm}\left[x_l-x_m+\frac{G_l(\omega+i\delta)}{\beta n_F(\varepsilon_l)[1-n_F(\varepsilon_l)]}-\frac{G_m(\omega+i\delta)}{\beta n_F(\varepsilon_m)[1-n_F(\varepsilon_m)]}\right] . \tag{6}$$

These equations determine [via (5) and (3b)] the changes $\delta\mu_l$ in (2a). Clearly, Eq. (6) must be solved before taking the dc limit. Anyway, the right-hand side of (6) results from the right-hand side of (4). The latter expression is, however, correct just to the lowest order in g since, e.g., the transition rate W_{mn} itself is just the lowest-order quantity (in g) which cannot be properly generalized to higher orders. Hence the standard approach is based on an expansion of quantities entering relevant kinetic equations in powers of g before performing the dc limit—this is the main point of our criticism here.

For a moment, let us assume the standard scheme of calculation of σ via (2a), (3b), (5), and (6). In view of (6), the Kasuya-Koide[1] result,

$$\sigma=\frac{\beta e^2}{2\Omega}\sum_{m,n}\sum_{\sigma}\Gamma_{mn}(x_m-x_n)^2+o(g^2)\ , \tag{7}$$

looks like an unphysical omission of the shifts $\delta\mu_l$, or like a consequence of the high-frequency solution of the low-frequency equation (6), or in other words, like the lowest-order iteration of (6) which becomes clearly incorrect in the dc limit.[3-5] Because of that, not (7) but (2), (3b), (5), and (6) became a starting point for all of the contemporary theory of phonon-assisted hopping. The situation did not change even though internal inconsistencies were found in the Markovian approach.[6] Moreover, a fully rigorous (though difficult to understand) derivation of the Kasuya-Koide result (7) appeared which starts from the Kubo formulas and preserves cautiously the correct order of limiting processes[7,8] ($\Omega\to+\infty$, $\omega+i\delta\to 0$, and then $g\to 0$). In the meantime, the result (7) was also surprisingly shown to agree with experiment,[7,9] and the starting equations of Miller and Abrahams (rate equations) (4) were shown to be incorrect in higher [crucial for the difference between (7) and (2a)] orders.[10] Nevertheless, the situation remained unchanged as no explicit error was found in the original physically transparent arguments [based on Markovian kinetic equations (4)] leading to (2a). The aim of the present work is to fill this gap, i.e., to derive (7) from the most general kinetic equations—the (time-convolution) generalized master equations (GME's), and to identify the crucial step responsible for the difference between (7) and (2a).

In principle, one can still argue in support of the standard reasoning, saying that we need mainly the lowest-order (in g) asymptotics of the dc conductivity. For that, it might seem sufficient to use just the lowest-order kinetic equations like (4). Recently, however, important lowest-order changes in transfer rates have been found which are caused by higher-order terms in the GME.[11-13] These changes can therefore yield relevant corrections even to the lowest-order dc conductivity formula. This observation is therefore an additional argument for reexamining this old problem by a new technique which uses no expansion in the kinetic equations and takes (if at all) the expansion in powers of g just at the end of calculation, after taking the dc limit.

II. STANDARD KINETIC EQUATION

Let us start from the Liouville equation for the density matrix $\rho(t)$ of the coupled electron-phonon system

$$\begin{aligned} i\frac{\partial}{\partial t}\rho(t)&=\frac{1}{\hbar}[H-\mathbf{d}\cdot\mathcal{E}(t),\rho(t)] \\ &\equiv L\rho(t)-\frac{1}{\hbar}\mathcal{E}(t)\cdot[\mathbf{d},\rho(t)]\ . \end{aligned} \tag{8}$$

Here $L=(1/\hbar)[H,\ldots]$ is the Liouville superoperator without electric field. As we are interested in the Ohmic conductivity, let us linearize (8) with respect to $\mathcal{E}(t)$. This means that we set

$$\begin{aligned} &\rho(t)=\rho_{\rm eq}+\delta\rho(t),\quad \rho_{\rm eq}=\frac{e^{-\beta H}}{{\rm Tr}(e^{-\beta H})}\ , \\ &\delta\rho(t)\to 0,\ t\to-\infty\quad \text{for } \mathcal{E}(t)\to 0,\ t\to-\infty \end{aligned} \tag{9}$$

in (8) and solve it up to the terms $\sim\mathcal{E}(t)$ in the Kubo[14] manner. Doing so, we get

$$D\delta\rho(t)=\frac{i}{\hbar}D\int_{-\infty}^{t}d\tau\, e^{-iL(t-\tau)}\mathcal{E}(\tau)\cdot[\mathbf{d},\rho_{\rm eq}]\ . \tag{10}$$

Here

$$(DA)_{\{m\mu\}\{n\nu\}}=\delta_{\{m\mu\}\{n\nu\}}p_{\{\nu\}}\sum_{\{\lambda\}}A_{\{m\lambda\}\{m\lambda\}} \tag{11}$$

is the Peier[15] projector on the "interesting" (or relevant) part of the information contained in A; A is an arbitrary operator, Latin (Greek) indices in curly brackets designate many-particle eigenstates of H_e ($H_{\rm ph}$), and $p_{\{\nu\}}$ is the Boltzmann weight factor of the phonon state $|\{\nu\}\rangle$. On the other hand, one may rewrite the linearized version of (8) as a set of two equations for $D\delta\rho(t)$ and $(1-D)\delta\rho(t)$ (Refs. 16-19):

$$\begin{aligned} i\frac{\partial}{\partial t}D\delta\rho(t)&=DLD\delta\rho(t)-\frac{1}{\hbar}\mathcal{E}(t)\cdot D[\mathbf{d},\rho_{\rm eq}] \\ &\quad+DL(1-D)\delta\rho(t)\ , \end{aligned} \tag{12a}$$

$$\begin{aligned} i\frac{\partial}{\partial t}(1-D)\delta\rho(t)&=(1-D)L(1-D)\delta\rho(t) \\ &\quad-\frac{1}{\hbar}\mathcal{E}(t)\cdot(1-D)[\mathbf{d},\rho_{\rm eq}] \\ &\quad+(1-D)LD\delta\rho(t)\ . \end{aligned} \tag{12b}$$

Solving (12b) for $(1-D)\delta\rho(t)$ yields

$$(1-D)\delta\rho(t)=-i\int_{-\infty}^{t}e^{-i(1-D)L(t-\tau)}(1-D)LD\delta\rho(\tau)d\tau+\frac{i}{\hbar}\int_{-\infty}^{t}\mathcal{E}(\tau)\cdot e^{-i(1-D)L(t-\tau)}(1-D)[\mathbf{d},\rho_{\rm eq}]d\tau\ . \tag{13}$$

In combination with (12a), it gives

$$\frac{\partial}{\partial t}D\delta\rho(t)=-iDLD\delta\rho(t)+\frac{i}{\hbar}\mathcal{E}(t)\cdot D[\mathbf{d},\rho_{\rm eq}]-\int_{-\infty}^{t}DLe^{-i(1-D)L(t-\tau)}(1-D)LD\delta\rho(\tau)d\tau$$
$$+\frac{1}{\hbar}\int_{-\infty}^{t}\mathcal{E}(\tau)\cdot DLe^{-i(1-D)L(t-\tau)}(1-D)[\mathbf{d},\rho_{\rm eq}]d\tau\ . \tag{14}$$

This is the operator form of the linearized time-convolution generalized master equations. It is clear that because of the common starting equation (8) and avoidance of any approximation (up to now), the explicit formula (10) is an exact solution to the complicated equation (14) for $D\delta\rho(t)$ as long as (13) applies. Nevertheless, the contemporary treatments of kinetic phenomena prefer kinetic equations of type (4) or (6), resulting from equations like (14), to explicit solutions like (10). This is the reason it is worth discussing first the connection between (14) and (4) or (6) for an elemental example of a single electron on a pair of states (dimer).

First, we use the identities

$$DLD=0,\quad L_0D=DL_0=0\ , \tag{15a}$$

with

$$L_0=\frac{1}{\hbar}[H_0,\dots],\quad H_0=H_e+H_{\rm ph}\ , \tag{15b}$$

and

$$D[d,\rho_{\rm eq}]=0\ . \tag{15c}$$

(The last identity is due to the currently assumed negligible role of the off-diagonal elements of the coordinate in the dc problem which may be exactly proved[7]—we shall also use this assumption in this work.) We then use the form of D in (11), take the lowest order term in g on the right-hand side of (14), and afterwards take the dc limit $\omega+i\delta\to 0$ in all the coefficients of the resulting equation. After some straightforward algebra, we obtain

$$-i(\omega+i\delta)\delta f_1^{\omega+i\delta}=W_{12}^{\rm eq}\delta f_2^{\omega+i\delta}-W_{21}^{\rm eq}\delta f_1^{\omega+i\delta}$$
$$+\beta(x_1-x_2)W_{21}^{\rm eq}f_1^{\rm eq}e\mathcal{E}^{\omega}\ ,$$
$$\delta f_2^{\omega+i\delta}=-\delta f_1^{\omega+i\delta}\ . \tag{16}$$

Here, the Fourier transformation

$$\delta f_i(t)=\int\frac{d\omega}{2\pi}e^{-i\omega t}\delta f_i^{\omega}\ ,$$
$$\delta f_i^{\omega}=\int dt\,e^{i\omega t}\delta f_i(t),\ \text{etc.}\ , \tag{17}$$

and the relation

$$\delta f_i(t)={\rm Tr}[\delta\rho(t)a_i^{\dagger}a_i]=\sum_{\{m\}}m_i\delta P_{\{m\}}(t) \tag{18}$$

have been used. The quantity $\delta P_{\{m\}}(t)$ is the field-induced change of the probability $P_{\{m\}}(t)=\sum_{\{\mu\}}\rho_{\{m\mu\}\{m\mu\}}$ of finding the electron configuration $\{m\}$. Equation (16) is physically equivalent to (6). The reason for a small difference in coefficients is that, in our situation, we have taken the kinematic correlations [ignored in (4) and (6)] exactly into account [if the electron is at site 1, it cannot be at site 2, and vice versa, so that (4) should be taken rather without the nonlinear terms $f_1(t)f_2(t)$]. From both (16) and (6), we find that $\delta f_i^{\omega+i\sigma}$ are regular (finite) and of the zeroth order in g after the dc limit is taken. These conclusions will be questioned below. Before going further, however, attention should be turned to the fact that, in order to get the correspondence between (14) and (6), the expansion in powers of g has (as usual) been and must necessarily be performed before taking the dc limit $\omega+i\delta\to 0$. In what follows, we will avoid such an unphysical step and look for the difference in final formulas thus obtained.

III. SOLUTION TO GME USING EQUATION (13)

It is a matter of simple algebra to show that once (13) applies, (10) is the solution to the linearized GME (14) which disappears when $t\to-\infty$. Hence, from (13) and (14), or equivalently (10),

$$\delta P_{\{m\}}(t)=\frac{i}{\hbar}\int_{-\infty}^{t}d\tau\sum_{\{\mu\}}\{e^{-iL(t-\tau)}$$
$$\times\mathcal{E}(\tau)\cdot[\mathbf{d},\rho_{\rm eq}]\}_{\{m\mu\}\{m\mu\}}\ . \tag{19}$$

After taking the Fourier transformation, this reads

$$\delta P_{\{m\}}^{\omega+i\delta}=-\mathcal{E}^{\omega}\cdot\frac{1}{\hbar}\sum_{\{\mu\}}\left[\frac{1}{\omega+i\delta-L}[\mathbf{d},\rho_{\rm eq}]\right]_{\{m\mu\}\{m\mu\}}\ . \tag{20}$$

Using the identity

$$\frac{1}{\omega+i\delta-L}=\frac{1}{\omega+i\delta-L_0}\left[1+\mathcal{L}\frac{1}{\omega+i\delta-L}\right],$$
$$\mathcal{L}=\frac{1}{\hbar}[\mathcal{H},\dots]\ , \tag{21}$$

we obtain from (20)

$$\delta P_{\{m\}}^{\omega+i\delta}=-\mathcal{E}^{\omega}\cdot\frac{1}{\hbar(\omega+i\delta)}\sum_{\{\mu\}}\left[\mathcal{L}\frac{1}{\omega+i\delta-L}[\mathbf{d},\rho_{\rm eq}]\right]_{\{m\mu\}\{m\mu\}}\ . \tag{22}$$

This result is formally singular in the dc limit. Because of the relation

$$\delta f_i^{\omega+i\delta}=\sum_{\{m\}} m_i \delta P_{\{m\}}^{\omega+i\delta} \ , \tag{23}$$

this means a contradiction with the result of (16) as well as (6). The real existence of this singularity may be most easily verified by calculating the coefficient in (22) with the correct order of limits:

$$\begin{aligned}
&\sum_{\{\mu\}}\left[\mathcal{L}\frac{1}{\omega+i\delta-L}[\mathbf{d},\rho_{\rm eq}]\right]_{\{m\mu\}\{m\mu\}} \\
&\quad=\int d\alpha\, d\beta \sum_{\{\mu\}}\left[\left\langle\{m\mu\}\left|\frac{1}{\hbar}\mathcal{H}\right|\alpha\right\rangle\frac{1}{\omega+i\delta-\frac{1}{\hbar}(E_\alpha-E_\beta)}\langle\alpha|[\mathbf{d},\rho_{\rm eq}]|\beta\rangle\langle\beta|\{m\mu\}\rangle\right. \\
&\qquad\left.-\langle\{m\mu\}|\alpha\rangle\frac{1}{\omega+i\delta-\frac{1}{\hbar}(E_\alpha-E_\beta)}\langle\alpha|[\mathbf{d},\rho_{\rm eq}]|\beta\rangle\left\langle\beta\left|\frac{1}{\hbar}\mathcal{H}\right|\{m\mu\}\right\rangle\right] \\
&\quad\xrightarrow[\omega+i\delta\to 0]{}\int d\alpha\, d\beta\sum_{\{\mu\}}\left[\left\langle\{m\mu\}\left|\frac{1}{\hbar}\mathcal{H}\right|\alpha\right\rangle\langle\alpha|[\mathbf{d},\rho_{\rm eq}]|\beta\rangle\langle\beta|\{m\mu\}\rangle\right. \\
&\qquad\left.-\langle\{m\mu\}|\alpha\rangle\langle\alpha|[\mathbf{d},\rho_{\rm eq}]|\beta\rangle\left\langle\beta\left|\frac{1}{\hbar}\mathcal{H}\right|\{m\mu\}\right\rangle\right]\frac{1}{-\frac{1}{\hbar}(E_\alpha-E_\beta)+i0^+} \\
&\quad=g^2\int d\alpha_0 d\beta_0\sum_{\{\mu\}}\left[\left\langle\{m\mu\}\left|\frac{1}{\hbar g}\mathcal{H}\right|\alpha_0\right\rangle\left\langle\alpha_0\left|\frac{1}{g}[\mathbf{d},\rho_{\rm eq}]\right|\beta_0\right\rangle\langle\beta_0|\{m\mu\}\rangle\right. \\
&\qquad\left.-\langle\{m\mu\}|\alpha_0\rangle\left\langle\alpha_0\left|\frac{1}{g}[\mathbf{d},\rho_{\rm eq}]\right|\beta_0\right\rangle\left\langle\beta_0\left|\frac{1}{\hbar g}\mathcal{H}\right|\{m\mu\}\right\rangle\right]\frac{1}{-\frac{1}{\hbar}(E_\alpha^0-E_\beta^0)+i0^+}+o(g^2) \\
&\quad=\sum_{\{\mu\}}\left[\mathcal{L}\frac{1}{-L_0+i0^+}[\mathbf{d},\rho_{\rm eq}]\right]_{\{m\mu\}\{m\mu\}}+o(g^2)\neq 0 \ .
\end{aligned} \tag{24}$$

Here $|\alpha\rangle, |\beta\rangle,\ldots \to |\alpha_0\rangle, |\beta_0\rangle,\ldots,$ as $g\to 0$ are the eigenstates of H (H_0) and $E_\alpha,\ldots$ ($E_\alpha^0,\ldots$) are the corresponding eigenenergies. Explicit calculation of the right-hand side of (24) then proves our statement. The existence of the singularity in $\delta P_{\{m\}}^{\omega+i\delta}$ in (22) does not, however, mean that measurable quantities $[P_{\{m\}}(t)]$ become singular. Only the Fourier components of derivatives of the probabilities with respect to the acting field become singular when $\omega+i\delta\to 0$. Nevertheless, we found that for arbitrarily small $g\neq 0$, the linearized probabilities and mean occupation numbers appreciably differ in the dc limit $[g^2/(\omega+i\delta)\to\infty$ in contrast to the standard Van Hove limit $g\to 0$, $\omega+i\delta\to 0$, $g^2/(\omega+i\delta)=$const] from those given by the standard treatment. Introducing then (22) and (24) into the Kubo[14] formula

$$\sigma=\lim_{\omega+i\delta\to 0}\frac{(-ie)(\omega+i\delta)}{\Omega}\sum_{j,\sigma}\delta f_j^{\omega+i\delta}x_j/\mathcal{E}^\omega \tag{25}$$

fully reproduces the Kasuya-Koide result (7) (which was originally derived as only approximate but is, as a matter of fact, exact[7,8]). In what follows, we are going to show that one obtains the same result also directly from GME (14) without invoking the relation (13). The necessary condition for that is, however, that the order of limiting processes cannot be interchanged, i.e., that the expansion in powers of g is either not performed at all or is performed only after taking the dc limit $\omega+i\delta\to 0$.

IV. DIRECT SOLUTION OF GME (14)

Equation (14) is nothing but the Nakajima[16] and Zwanzig[17–19] identity for the density matrix of the system in the time-dependent external field

$$\begin{aligned}
\frac{\partial}{\partial t}D\rho(t)&=-iDL'(t)D\rho(t)-\int_{t_0}^{t}DL'(t)\exp_{\leftarrow}\left[-i\int_\tau^t(1-D)L'(\tau')d\tau'\right](1-D)L'(\tau)D\rho(\tau)d\tau \\
&\quad-iDL'(t)\exp_{\leftarrow}\left[-i\int_{t_0}^{t}(1-D)L'(\tau)d\tau\right](1-D)\rho(t_0),\quad L'(t)=L-\frac{1}{\hbar}\mathcal{E}(t)\cdot[\mathbf{d},\ldots] \ ,
\end{aligned} \tag{26}$$

linearized with respect to $\mathcal{E}(t)$ and taken in the limit $t_0\to-\infty$. With $\mathcal{E}=0$ and for D given by (11), (26) is equivalent

to the standard GME

$$\frac{\partial}{\partial t}P_{\{m\}}(t)=\sum_{\{n\}(\neq\{m\})}\int_{t_0}^{t}[w_{\{m\}\{n\}}(t-\tau)P_{\{n\}}(\tau)-w_{\{n\}\{m\}}(t-\tau)P_{\{m\}}(\tau)]d\tau+J_{\{m\}}(t,t_0)\ . \tag{27}$$

In (27),

$$w_{\{m\}\{n\}}(\tau)=-\sum_{\{\mu\},\{\nu\}}(\mathcal{L}e^{-i(1-D)L\tau}\mathcal{L})_{\{m\mu\}\{m\mu\}\{n\nu\}\{n\nu\}}p_{\{\nu\}} \tag{28}$$

are the usual memory functions and

$$J_{\{m\}}(t,t_0)=-i\sum_{\{\mu\}}[\mathcal{L}e^{-i(1-D)L(t-t_0)}(1-D)\rho(t_0)]_{\{m\mu\}\{m\mu\}} \tag{29}$$

is the initial condition term. GME's (26) and (27) are useful for describing time evolution of open systems. It is worth mentioning that similar convolution-type equations could also be obtained from, e.g., the Mori scheme,[20] using the set of observables $a^{\dagger}_{m\sigma}a_{m\sigma}$. Here, before proceeding further, it is worth mentioning that converting the order of limiting processes, i.e., first expanding (as usual) $w_{\{m\}\{n\}}$ to the second order in g and performing the limit $\omega+i\delta\to 0$ afterwards yields

$$w^{\omega+i\delta}_{\{m\}\{n\}}\equiv\int_0^{+\infty}w_{\{m\}\{n\}}(\tau)e^{i(\omega+i\delta)\tau}d\tau \underset{\omega+i\delta\to 0}{\sim} W^{\mathrm{eq}}_{\{m\}\{n\}}\ . \tag{30}$$

Here $W^{\mathrm{eq}}_{\{m\}\{n\}}$ is the lowest-order golden-rule Markovian transition rate. This then leads to Eq. (4) and all the theory returns to the Markovian lowest-order form leading to (2a) and (2b). In connection with our discussion of (16), we can therefore conclude that avoiding the unphysical (but standard) expansion in powers of g before performing the dc limit in our approach is the reason our result (7) for the dc conductivity σ differs from the standard lowest-order Markovian result (2a). On the other hand, this is the reason it fully agrees with a form of the theory starting from the Kubo formulas which avoids any expansion in powers of g before performing the dc limit (see, e.g., Refs. 7 and 8 in contrast to, e.g., Refs. 3–5, 21, and 22).

Taking the Fourier transformation (17) turns the linearized GME to the form

$$(\omega+i\delta)D\delta\rho^{\omega+i\delta}=DLD\delta\rho^{\omega+i\delta}-\frac{1}{\hbar}\mathcal{E}^{\omega}\cdot D[\mathbf{d},\rho_{\mathrm{eq}}]+DL[\omega+i\delta-(1-D)L]^{-1}(1-D)\left[LD\delta\rho^{\omega+i\delta}-\frac{1}{\hbar}\mathcal{E}^{\omega}\cdot[\mathbf{d},\rho_{\mathrm{eq}}]\right]$$
$$=DL\delta\rho^{\omega+i\delta}-\frac{1}{\hbar}\mathcal{E}^{\omega}\cdot D[\mathbf{d},\rho_{\mathrm{eq}}]-iDLA^{\omega+i\delta}\ . \tag{31a}$$

Here, we introduced

$$A^{\omega+i\delta}=i[\omega+i\delta-(1-D)L]^{-1}(1-D)\times\left[LD\delta\rho^{\omega+i\delta}-\frac{1}{\hbar}\mathcal{E}^{\omega}\cdot[\mathbf{d},\rho_{\mathrm{eq}}]\right]-i(1-D)\delta\rho^{\omega+i\delta}\ . \tag{31b}$$

From the definition (31b), we get

$$[\omega+i\delta-(1-D)L]A^{\omega+i\delta}=i(1-D)\left[L\delta\rho^{\omega+i\delta}-\frac{1}{\hbar}\mathcal{E}^{\omega}\cdot[\mathbf{d},\rho_{\mathrm{eq}}]-(\omega+i\delta)\delta\rho^{\omega+i\delta}\right], \tag{32}$$

so that

$$(\omega+i\delta)(1-D)\delta\rho^{\omega+i\delta}=(1-D)\left[L\delta\rho^{\omega+i\delta}-\frac{1}{\hbar}\mathcal{E}^{\omega}\cdot[\mathbf{d},\rho_{\mathrm{eq}}]\right]+i[\omega+i\delta-(1-D)L]A^{\omega+i\delta}\ . \tag{33}$$

Summing this equation and the linearized GME (31a) yields

$$(\omega+i\delta)\delta\rho^{\omega+i\delta}=L\delta\rho^{\omega+i\delta}-\frac{1}{\hbar}\mathcal{E}^{\omega}\cdot[\mathbf{d},\rho_{\mathrm{eq}}]+i(\omega+i\delta-L)A^{\omega+i\delta}\ . \tag{34}$$

This means that the Fourier-transformed linear change of the density matrix

$$\delta\rho^{\omega+i\delta}=-\frac{1}{\hbar}(\omega+i\delta-L)^{-1}\mathcal{E}^{\omega}\cdot[\mathbf{d},\rho_{\mathrm{eq}}]+iA^{\omega+i\delta}\ . \tag{35}$$

From (31b), it follows that

$$DA^{\omega+i\delta}=0 , \tag{36}$$

so that (35) gives finally

$$D\delta\rho^{\omega+i\delta}=-\frac{1}{\hbar}D(\omega+i\delta-L)^{-1}\mathcal{E}^{\omega}\cdot[\mathbf{d},\rho_{\mathrm{eq}}] . \tag{37}$$

Now, we use the form of D given by (11). The off-diagonal elements are then zero on both sides of (37) while the diagonal elements yield (20). Therefore (19) is the solution to the linearized GME (14). As we have still performed no approximation, this solution is exact to any power of g. The derivation of the dc conductivity formula (7) is then the same as in the previous section.

A few words are worth mentioning here regarding the physical significance of our exact solution (37). In the first equality of (31a) (i.e., in the linearized Fourier-transformed GME), let us as usual (a) assume that (15a) and (15c) apply and (b) put, as in the standard treatment,

$$\frac{1}{\omega+i\delta-(1-D)L}\approx\frac{1}{\omega+i\delta-L_0}\approx\frac{1}{\omega+i\delta-L} \tag{38}$$

(which is formally correct to the lowest order in g provided that $\omega+i\delta\neq 0$). After using the standard approximation (38), Eq. (31a) reproduces our general and exact solution (37) provided that we ignore (by definition) the term

$$P\delta\rho^{\omega+i\delta}\equiv DL[\omega+i\delta-(1-D)L]^{-1}(1-D)LD\delta\rho^{\omega+i\delta} .$$

However, it is to be stressed that it is just this term which is responsible for the terms with $\delta\mu_r$ in (2a) and those with $G_r(\omega+i\delta)$ on the right-hand side of (6). Hence, in order to get results corresponding to our exact solution (37), any use of the approximation like (38) in the kinetic equations (as is common in the standard theories) must necessarily be followed by ignoring the field-induced changes $\delta\mu_r$ in (2a) and the terms $\sim G_r(\omega+i\delta)$ on the right-hand side of (6). This then turns the Miller and Abrahams result (2) to the Kasuya-Koide formula (7). On the other hand, since the terms like $P\delta\rho^{\omega+i\delta}$ are currently not ignored in the standard theories but (38) is still used, the usual result for $\delta P^{\omega+i\delta}_{\{m\}}$ and hence the dc conductivity σ (2a) appreciably differs from the exact result (22) and (7), and cannot therefore serve as a sound basis for further discussion.

V. CONCLUSIONS

We have shown that by keeping, with meticulous care, the correct order of limiting processes ($\Omega\rightarrow+\infty$, $\omega+i\delta\rightarrow 0$, and then contingently $g\rightarrow 0$), the kinetic equations (in the form of the most general generalized master equations) yield the same explicit result (7) for the dc conductivity σ as the theory based on the Kubo formulas with the same order of limits, i.e., without expansion in powers of g before performing the dc limit on, e.g., the right-hand side of the equations of motion. We have also illustrated that the latter (standard but unphysical) expansion turns the theory to the usual Markovian form. This suggests that the long-past (but fully ignored) warning by Peier[15] that the Markov-Born approximation [leading to (4)] to the GME cannot be used in the dc limit was probably right. In other words, the kinetic stage of the development [where the standard kinetic equations like (4) do probably apply] cannot be extended up to the zero frequency. The fact that we do not have the free relaxation but rather the relaxation under the influence of the electric field in our situation makes no difference, as we could also discuss the problem via the Einstein relations and free diffusion in space.

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