Calculation of the Frequency-Dependent Photoconductivity of Organic Molecular Crystals

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The frequency dependent photoconductivity of charge carriers in organic molecular crystals is derived using general connections of the velocity autocorrelation function to the mean-square-displacement of the charge carriers and to the memory function of generalized master equations. The dynamics of the charge carriers is described by a stochastic Liouville equation, in one case in the usual Markovian form and in the other in a generalized non-Markovian form.

1. Introduction

The aim of this paper is to derive explicit expressions for the frequency-dependent photoconductivity of organic molecular crystals. To that end we describe the dynamics of the charge carriers by stochastic Liouville equations (SLE) and use general connections of the velocity autocorrelation function to the mean-square-displacement of the charge carriers and to the memory functions of generalized master equations which have been derived in the previous paper in this journal.

On the basis of linear response theory [1] the mobility of a charge carrier, and thus the conductivity, may be expressed by the velocity autocorrelation function $\psi_{ve}(t)$ in the following way:

$$\sigma'(\omega) = \frac{i}{2} f(\omega); \quad \sigma''(\omega) = \mathcal{P} \int \frac{d\omega'}{\pi} \frac{\sigma(\omega')}{\omega' - \omega}. \quad (1.2.1)$$

$$f(\omega) = E_{\rho}(\omega)^{-1} \int_{-\infty}^{\infty} dt \ e^{-i\omega t} \psi_{ve}(t). \quad (1.2.2)$$

In this expressions $\sigma'(\omega)$ and $\sigma''(\omega)$ are the real and imaginary parts of the conductivity, the universal prefactor $E_{\rho}(\omega)$ reduces to $kT$ in the high temperature limit, and the notation (1.2.1) means (2.1) of [2], which furtheron will be denoted as I. In that paper a connection between $\psi_{ve}(t)$ and the mean-square-displacement of the charge carrier has been established, generalizing in this way a result of Scher and Lax [3].

\begin{equation}
\psi_{ve}(t) = \frac{1}{2} \frac{d^2}{dt^2} \text{Tr} \rho (\hat{x}(t) - \hat{x})^2.
\end{equation}

An alternative way of expressing this result is

\begin{equation}
\psi_{ve}(t) = \frac{1}{2} \frac{d^2}{dt^2} \sum_m \sum_n (m-n)^2 p_m^n(t)
\end{equation}

where the probability $p_m^n(t)$ of finding the particle at time $t$ at site $m$ is given by

\begin{equation}
p_m^n(t) = \langle m | \hat{\rho}(t) | m \rangle
= \langle m | e^{-i\mathcal{L} t} | n \rangle \langle n | \rho | m \rangle.
\end{equation}

$m$ is a set of localized basis vectors, $\mathcal{L}$ the Liouville operator of the system, and $\rho$ its canonical density operator. It is important that this probability has to be calculated with the initial condition

\begin{equation}
\langle a | \hat{\rho}(0) | b \rangle = \frac{1}{2} \langle a | \rho | b \rangle (\delta_{a,n} + \delta_{b,n})
\end{equation}

i.e., that the density operator $\hat{\rho}(t)$ has non-diagonal matrix elements at the initial time.

In the limit of high temperatures the velocity autocorrelation function may be expressed by the memory function $\hat{W}(k,t)$ of a generalized master equation:

\begin{equation}
\psi_{ve}(t) = \frac{1}{2} \left( \frac{\partial^2 \hat{W}(k,t)}{\partial k^2} \right)_{k=0}.
\end{equation}

In the following we shall use these results in order to calculate for organic molecular crystals the mobility of charge carriers generated by photoexcitation. To
that end in Sect. 2 and 3 below the dynamics of the charge carriers is described by a stochastic Liouville equation. In Sect. 2 the Markovian Form of the SLE, which has proven successful in describing the coupled bandlike and hopping motion of excitons [4–6] is used. In Sect. 3 the non-Markovian generalization of this SLE suggested by Kenkre [7] is used. The results are summarized and discussed in the final Sect. 4.

2. Calculation of the Photoconductivity

It is known that electron motion in organic molecular crystals such as naphthalene and anthracene has aspects both of band (coherent) transport and hopping (incoherent) transport. The coexistence of these two types of motion is particularly clear in the light of the transition observed by Schein et al. [8, 9] which marks the change-over in the dominant type of motion. It is therefore natural to approach the calculation of the conductivity with the help of a transport equation capable of describing both coherent and incoherent motion. The stochastic Liouville equation (SLE) is a transport entity especially designed for this purpose. It has been derived stochastically [4–6] and used extensively in exciton transport by Haken and Reineker (for references see [10]) and others [11]. It has also been developed dynamically by Haken and Reineker [12], Grover and Silbey [13], and others [14, 15] on the basis of a microscopic model [16–18]. It describes the evolution of the density matrix \( \rho \) of each of the \( N \) non-interacting particles through

\[
\frac{\partial \rho_{nn}}{\partial t} = -i \sum_r (H_{mr} \rho_{rn} - H_{rn} \rho_{mn})
+ 2 \delta_{m,n} \sum_r (\gamma_{mr} \rho_{rr} - \gamma_{rm} \rho_{nm})
- (1 - \delta_{m,n}) 2 \Gamma \rho_{mn} + (1 - \delta_{m,n}) 2 \tilde{\gamma}_{m,n} \rho_{nm}.
\] (2.1)

The microscopic derivation [12–15] of (2.1) and a study [7] of its relation to other ways of describing transport has shown that \( \gamma_{mr} \)'s are transfer rates arising typically (although not necessarily) from the phonon-assisted part of the interaction, \( H_{mr} \)'s are Hamiltonian matrix elements arising from the part not so assisted and form the “polaron” bandwidth, and \( \Gamma = \sum_m \gamma_{mm} \) is a rate of destruction of off-diagonal elements of \( \rho \) and arises from site energy fluctuations and fluctuations of the interaction matrix elements. The final term on the right hand side of (2.1) may more easily be discussed in a representation of Bloch and not of localized states. It can be shown that \( \Gamma \) is an overall scattering rate for all \( k \)-states, whereas the \( \gamma \)'s of the last term describe scattering rates which are different for different \( k \)-states. For that reason this term is less simple to handle mathematically. Some authors [7, 11] have dropped this term. In Subsect. 2.1 below where we demonstrate the calculation of the velocity autocorrelation function \( \varphi_v(t) \) and the conductivity from the memory function of the GME [19, 20] corresponding to (2.1) in nearest neighbour approximation, we shall adopt this procedure for simplicity. There is, however, no need for this approximation, which employs the memory function obtained by Kenkre [23, 24] for the simplified SLE, since the memory function of the full equation (2.1) with nearest neighbour interactions has been determined by Kühne and Reineker [21, 22].

2.1. Conductivity in the High Temperature Approximation

If we make the approximation that the \( H_{mr} \) and \( \gamma_{mr} \) are nearest-neighbour in character, the simplified SLE has the form

\[
\frac{\partial \rho_{mn}}{\partial t} = -i H_1 (\rho_{m+1,n} + \rho_{m-1,n} - \rho_{m,n+1} - \rho_{m,n-1})
+ \delta_{m,n} 2 \gamma_1 (\rho_{m+1,m+1} + \rho_{m-1,m-1} - 2 \rho_{mm})
- (1 - \delta_{m,n}) 2 \Gamma \rho_{mn}.
\] (2.2)

The results of Sect. 2.2 of I. suggest that the calculation of the conductivity can be carried out using (1.2,10), which connects the memory functions to the velocity autocorrelation function and (1.2,1) and (1.2,2) which relate the latter to the conductivity. The memory function corresponding to (2.2) has been given by Kenkre [23, 24]

\[
\varphi_{m,n}(t) = 4 \gamma_{m,n} \delta(t)
+ 2 H_1^2 e^{-2 t \Gamma} (J_{m,n+1}^2 + J_{m,n-1}^2 + 2 J_{m,n+1} J_{m,n-1})
- 2 J_{m,n}^2
\] (2.3)

where the argument of the Bessel functions is \( 2 H_1 t \).

Equation (2.3) may be written in the more compact form [25]

\[
\varphi_{m,n}(t) = 4 \gamma_{m,n} \delta(t) + \frac{e^{-2 t \Gamma}}{\Gamma} \frac{d}{dt} J_{m,n}^2 (2 H_1 t).
\] (2.4)

The Fourier transform of this expression is [23, 25]

\[
\varphi(k,t) = -16 \gamma_1 \sin \frac{k}{2} \delta(t) + \frac{e^{-2 t \Gamma}}{\Gamma} \frac{d}{dt} \left( 4 H_1 t \sin \frac{k}{2} \right)
\] (2.5)

Equation (1.2,10) therefore immediately yields the velocity correlation function

\[
\psi_v(t) = 4 \gamma_1 \delta(t) + 2 H_1^2 e^{-2 t \Gamma}.
\] (2.6)
This is a remarkably simple result. From (1.2.2) and (1.2.1) we get the real part of the conductivity as

\[
\sigma(\nu) = \frac{1}{E^*_\nu(\nu)} \left( 2 \gamma_1 + 2 H_1^2 \frac{2 \Gamma}{\omega^2 + (2 \Gamma)^2} \right). \tag{2.7}
\]

The imaginary part of the conductivity is obtained from (1.2.1) and the d.c. conductivity becomes

\[
\sigma(0) = \beta \left( 2 \gamma_1 + \frac{H_1^2}{\Gamma} \right). \tag{2.8}
\]

2.2. Conductivity for Arbitrary Temperatures

The calculation of the conductivity in Subsect. 2.1 above was carried out from (1.2.10) through the memory functions obtained in [23]. It required two assumptions: that the approximate SLE (2.2) was an adequate representation of the exact SLE (2.1) and that the approximate relation (1.2.10) between \( \psi_\nu(t) \) and the memory function was valid. We now refrain from making either of these assumptions. This will be done with the help of the exact relations (1.2.1,2) between the Fourier transform of \( \psi_\nu(t) \) and the mean-square-displacement for the special initial condition (1.2.5). For arbitrary initial conditions the mean-square-displacement calculated from (2.1) has been given in (11) of [26]. It is

\[
\langle m^2(t) \rangle = \langle m^2(0) \rangle + \sum_m (2m^2 \gamma_m + m^2 A_m) t \\
+ \sum_m \frac{1}{2} (m^2 A_m + m B_m - \sum_{m' \neq m} m m' C_{mm'}) \\
\cdot (\Gamma + \gamma_m)^{\frac{1}{2}} \left( e^{-2(\Gamma + \gamma_m)t} - 1 \right) \\
+ \sum_{m \neq m'} \frac{1}{2} m m' C_{mm'} (\Gamma - \gamma_{m+m})^{-1} (e^{-2(\Gamma - \gamma_{m+m})t} - 1).
\tag{2.9}
\]

\( \langle m^2(0) \rangle \) is the mean-square-displacement at the initial time and the following abbreviations have been introduced:

\[
A_m = H_m^2 (\Gamma + \gamma_m)^{-1}, \tag{2.10}
\]

\[
B_m = H_m V_m(0), \tag{2.11}
\]

\[
C_{mm'} = (\gamma_{m+m} + \gamma_m)^{-1} H_m H_{m'} W_{m+m}(0). \tag{2.12}
\]

\[
V_m(0) = i \sum_n (2n+m)(\rho_{n,n+m}(0) - \rho_{n+m,n}(0)) \tag{2.13}
\]

\[
W_m(0) = \sum_n (\rho_{m,n+m}(0) + \rho_{n+m,n}(0)) \tag{2.14}
\]

are determined from the initial value of the density operator according to (1.2.16).

Taking into account the twofold time derivative of the mean-square-displacement in the evaluation of the Fourier integral (1.2.2), we get

\[
E^*_\nu(\nu) = \sum_m (2m^2 \gamma_m + m^2 A_m) - \sum_m (2m^2 + m B_m - \sum_{m' \neq m} m m' C_{mm'}) \frac{\omega^2}{\omega^2 + 4(\Gamma + \gamma_m)^2} \\
- \sum_{m \neq m'} \frac{1}{2} m m' C_{mm'} \frac{\omega^2}{\omega^2 + 4(\Gamma - \gamma_{m+m})^2}. \tag{2.15}
\]

The inversion of (1.2.2) then yields the following expression for the velocity autocorrelation function:

\[
\psi_\nu(t) = \sum_m (2m^2 \gamma_m - \frac{1}{2} m B_m) \delta(t) \\
+ \sum_m \left( m^2 A_m + \frac{m}{2} B_m - \frac{1}{2} \sum_{m' \neq m} m m' C_{mm'} \right) \\
\cdot (\Gamma + \gamma_m)^{\frac{1}{2}} e^{-2(\Gamma + \gamma_m)t} \\
+ \sum_{m \neq m'} \frac{1}{2} m m' C_{mm'} (\Gamma - \gamma_{m+m}) e^{-2(\Gamma - \gamma_{m+m})t}. \tag{2.16}
\]

The conductivity is finally obtained from (1.2.1). It is clear that for a localized initial condition, i.e., for high temperatures, a vanishing result is obtained from (2.13) and \( W_m(0) \), being \( 2 \delta_{m,0} \) from (2.14), makes no contribution to (2.15). If we furthermore use the high temperature approximation also in the prefactor \( E^*_\nu(\nu) \), we obtain for the real and imaginary parts of the conductivity:

\[
\sigma'(\nu) = \beta \left( \sum_m m^2 \gamma_m + \sum_m m^2 H_m^2 \frac{2(\Gamma + \gamma_m)}{\omega^2 + 4(\Gamma + \gamma_m)^2} \right) \tag{2.17}
\]

\[
\sigma''(\nu) = -\beta \sum_m H_m^2 \frac{\omega}{\omega^2 + 4(\Gamma + \gamma_m)^2}. \tag{2.18}
\]

Considering the case of nearest neighbour interaction, we arrive at

\[
\sigma'(\nu) = \beta \left( 2 \gamma_1 + 2 H_1^2 \frac{2(\Gamma + \gamma_1)}{\omega^2 + 4(\Gamma + \gamma_1)^2} \right) \tag{2.19}
\]

\[
\sigma''(\nu) = -\beta 2 H_1^2 \frac{\omega}{\omega^2 + 4(\Gamma + \gamma_1)^2}. \tag{2.20}
\]

Finally the d.c. conductivity is given by

\[
\sigma(0) = \beta \left( 2 \gamma_1 + \frac{H_1^2}{\Gamma + \gamma_1} \right). \tag{2.21}
\]

The last expression is essentially (16) of [21] written in a simpler way. In the limit \( \omega \to 0 \) the prefactor \( E(\omega) \to \beta^{-1} \); therefore as regards the temperature dependent prefactor, the validity of (2.21) is not limited to high temperatures. On the other hand, in going from (2.12) to (2.21) we have used the diagonal initial density operator. However, from (2.12) it is immediately seen that for \( \omega = 0 \) the terms stemming from the non-diagonal part of the density operator disappear. Therefore (2.21) is correct for all temperatures.
Finally we consider the correlation function (2.16) also in the case of nearest neighbour interaction. It may be written in the following way:

\[
\psi_{ee}(t) = 4\gamma_1 \delta(t) + 2H_2^2 e^{-2(T + \gamma_1)t} - H_1V_1(0)\delta(t) + \left( H_1^2W_2(0) - \frac{H_1^2W_2(0)}{\gamma_1} \right) \cdot \frac{(T + \gamma_1)}{\gamma_1} e^{-2(T + \gamma_1)t} + \frac{H_1^2G}{\gamma_1} W_2(0) e^{-2Gt}.
\] (2.22)

The comparison with (2.6) shows that the terms in the first row are obtained from the approximate diagonal initial condition and may be written as

\[-\frac{1}{2}(\delta^2 \hat{W} / \delta k^2)_{k=0}.\]

The remaining terms are the additional contribution, if the exact initial condition (1.2,16) is used.

3. Results from a Generalized Non-Markovian Stochastic Liouville Equation

We have seen that according to (2.6, 7) and (2.17, 19, 21, 22) the correlation function as well as the conductivity splits into two parts corresponding exactly to the two term diffusion constant derived and discussed [5, 7, 13] earlier in the context of exciton transport. Needless to say that diffusion constant and the conductivity obtained above are related to each other through the Einstein relation.

Two curious features about the results we have obtained above require careful discussion. The first is that the conductivity in (2.19) has an unphysical constant component \( \beta_2 \gamma_1 \) which is non-vanishing at all frequencies. The second concerns the fact that if we put \( H_1 = 0 \) in (2.2), the resulting equation is equivalent to the simple Master equation

\[
\frac{dP}{dt} = 2\gamma_1(P_{m+1} + P_{m-1} - 2P_m)
\] (3.1)

and gives the well-known mean-square-displacement

\[
\langle m^2(t) \rangle = 4\gamma_1 t,
\] (3.2)

which may be also immediately deduced from (2.9). Equation (1.2,5), which states that the second time derivative of \( \langle m^2(t) \rangle \) is proportional to \( \psi_{ee}(t) \), therefore predicts that \( \psi_{ee}(t) \) and hence the conductivity vanishes for (3.1). However, when we put \( H_1 = 0 \) in (2.19), we get \( \beta_2 \gamma_1 \) as the conductivity. It appears reasonable that (3.1) should result in zero conductivity because the stimulus operator \( \hat{x} \) is diagonal in the \( |m\rangle \) representation. Yet our analysis above clearly shows that \( \beta_2 \gamma_1 \) is the conductivity for this case. This latter conclusion is also compatible with the two-term diffusion constant obtained earlier.

This apparent paradox and the unphysical \( \omega \)-independence of a part of \( \sigma(\omega) \) in (2.19) arise from the same source. Their resolution is found in certain general comments made by Kenkre [7] in his analysis of the SLE. It was pointed out by him that (2.1) or (2.2) is valid only for long times, that it predicts incorrect values of various quantities at short times including that of \( \frac{d}{dt} \langle m^2(t) \rangle \) and that this can lead to inconsistencies and even wrong values of the diffusion constant if blind use is made of the equation. These features arise from the partial Markovian approximation inherent in (2.1) or (2.2), whereby a part of the memory function corresponding to the equation is replaced by a delta-function in time [7]. This part is the \( g(t) - 1 \) of Grover and Stibey [13] or the correlation function of the local fluctuations \( \langle \hat{h}_{m_0}(0) \hat{h}_{m_0}(t) \rangle \) of Haken and Reineker [4-6]. When integrated once w.r.t. time it gives a constant under the delta-function approximation and when integrated once more it therefore results in the expression (3.2) showing proportionality to \( t \). However, in going back to it by differentiating (3.2) twice one gets a vanishing result if one forgets that (except for constant factors) \( \gamma_1 \) is an approximation to \( \int_0^\infty dt' (g(t') - 1) \).

The actual prediction for \( \psi_{ee}(t) \) made by (2.2) is therefore indeed (2.6) and the corresponding a.c. and d.c. conductivities are determined by (2.7) and (2.8). The respective terms \( \gamma_1 \delta(t) \) and \( \gamma_1 \) in (2.6) and (2.7) are, however, approximations which are a direct consequence of the partial Markovian approximation basic to (2.1) or (2.2). These results obtained from (2.2) through the memory functions (2.3, 4) and the relation (1.2,10) cease to clash with those obtained through expressions for \( \langle m^2(t) \rangle \) derived earlier [5, 13, 23] and the relation (1.2,13), as soon as we realized the existence of the delta-functions lurking beneath the surface in the latter.

The above discussion also makes it clear how an improved frequency dependence of \( \sigma(\omega) \) may be calculated. The generalization of the SLE suggested by Kenkre [7], which unmakes the partial Markovian approximation inherent in (2.1) or (2.2), is all that is required. The required form is in fact present in the original derivations [4-6, 12-15] of the SLE and all that we need to do is to refrain from replacing the actual time dependence of the relevant quantities by delta-functions. In the manner of (6) and (7) of [7] we therefore start with

\[
\frac{d}{dt} \rho_{mn} = -i \sum_r (H_{mr} \rho_{rn} - H_{rn} \rho_{mr}) + 2 \delta_{mn} \int_0^t dt' \sum_r (\gamma_{m' r'}(t-t') \rho_{r' r}(t') - \gamma_{r' m'}(t-t') \rho_{mr}(t'))
\]
\begin{align}
\frac{d}{dt} \langle m^2(t) \rangle &= 2 \sum_m m'^2 \int_0^t dt' \gamma_m(t') \\
- \frac{1}{2} \sum_m H_m V_m(t) \\
+ \frac{1}{2} \sum m H_m V_m(0) \\
- \sum_{m \neq m'} \frac{m m' H_m H_{m'} W_{m+m'}(0)}{(z + 2(\Gamma + \gamma_m))(z + 2(\Gamma + \gamma_{m'}))} \\
\end{align} 
(3.4)

\begin{align}
\frac{d}{dt} V_m(t) &= -2 \int_0^t dt' (\Gamma(t-t') + \gamma_m(t-t') V_m(t') \\
- 4m H_m + \sum m' H_{m'} W_{m+m'}(t) \\
- 4m H_m + \sum m' H_{m'} W_{m+m'}(t) \\
\end{align} 
(3.5)

\begin{align}
\frac{d}{dt} W_m(t) &= -2 \int_0^t dt' (\Gamma(t-t') - \gamma_m(t-t') W_m(t'). \\
\end{align} 
(3.6)

Laplace-transforming (3.4–6) we obtain \( \langle \gamma_m(z) \rangle \) is the Laplace-transform of \( \gamma_m(t) \), etc.

\begin{align}
\langle m^2(z) \rangle &= \left\langle \frac{m^2(0)}{z} \right\rangle + \frac{2}{z^2} \sum m'^2 \left( \gamma_m(z) \\
+ \frac{H_m^2}{z + 2(\Gamma + \gamma_m(z))} \right) - \frac{1}{2z} \sum m' H_m V_m(0) \\
- \sum_{m \neq m'} \frac{m m' H_m H_{m'} W_{m+m'}(0)}{(z + 2(\Gamma + \gamma_m))(z + 2(\Gamma + \gamma_{m'}))} \\
\end{align} 
(3.7)

From (1.2.2) and (1.2.5) we get \( (\varepsilon = 0^+ \rangle 
\begin{align}
f(\omega) &= -\frac{\omega^2}{2E_p(\omega)} \left( \langle m^2(-i\omega + \varepsilon) \rangle + \langle m^2(i\omega + \varepsilon) \rangle \right). \\
\end{align} 
(3.8)

The real and imaginary parts of the conductivity are finally obtained from (1.2.1).

To simplify the result we now assume the localized initial condition, i.e., \( \rho_m = \delta_{m,0} \delta_{m,\ast} \), as after (2.16).

Assuming furthermore that only nearest neighbour interaction is important, we obtain

\begin{align}
\langle m^2(z) \rangle &= \frac{4}{z^2} \left( \gamma_1(z) + \frac{H_1^2}{z + 2(\Gamma + \gamma_1(z))} \right). \\
\end{align} 
(3.9)

This gives, using (3.8),

\begin{align}
f(\omega) &= \frac{2}{E_p(\omega)} \left\{ \gamma_1(i\omega) + \gamma_1(-i\omega) \\
+ H_1^2 \left( \frac{1}{i\omega + 2(\Gamma + \gamma_1(i\omega))} \right) \right\} \left( \frac{1}{i\omega + 2(\Gamma - i\omega) + \gamma_1(-i\omega)} \right). \\
\end{align} 
(3.10)

Assuming now that, again for simplicity, \( \gamma(t), \Gamma(t) \) and \( \Gamma(t) \) depend on time in the same way

\begin{align}
\left\{ \begin{array}{l}
\gamma_1(t) \\
\gamma_1(t) \\
\Gamma(t)
\end{array} \right\} = \alpha e^{-a(t)} \left\{ \begin{array}{l}
\gamma_1 \\
\gamma_1 \\
\Gamma
\end{array} \right\} \\
\end{align} 
(3.11)

we obtain

\begin{align}
f(\omega) &= \frac{2}{E_p(\omega)} \left\{ \frac{2\gamma_1 \alpha^2}{\omega^2 + \alpha^2} \\
+ H_1^2 \left( \frac{4\alpha^2 \Gamma + \gamma_1}{\omega^4 + \omega^2(\alpha^2 - 4\alpha(\Gamma + \gamma_1)) + 4\alpha^2(\Gamma + \gamma_1)^2} \right) \right\}. \\
\end{align} 
(3.12)

From this result it is obvious that \( f(\omega) \) disappears with increasing frequency, which is in contrast to the conductivity derived from (2.15). In the d.c. case we immediately come back to (2.21).

The time dependence (3.11) results in the following expression for the correlation function:

\begin{align}
\psi_{ee}(t) &= 2\gamma_1 \alpha e^{-a(t)} \left\{ \frac{\Gamma + \gamma_1}{\alpha^2} \right\} \left\{ \frac{e^{\Gamma t} - e^{\gamma_1 t}}{z_1 - z_2} \right\} \\
+ 2H_1^2 \alpha \left\{ \frac{z_1 e^{\Gamma t} - z_2 e^{\gamma_1 t}}{z_1 - z_2} \right\}. \\
\end{align} 
(3.13)

where

\begin{align}
\frac{z_1}{z_2} = -\alpha + \frac{\sqrt{\alpha^2 - 4\alpha(\Gamma + \gamma_1)}}{2}. \\
\end{align} 
(3.14)

Also in this expression the \( \delta \)-function behaviour of (2.6) has disappeared.

4. Discussion

The results of this paper, which are of direct experimental interest, concern the a.c. and d.c. conductivity of organic molecular crystals. Our analysis is based on the stochastic Liouville equation description of electron transport in these crystals. This equation has been derived, analysed, generalized and utilized in the excitation context [4–7, 10–12, 21–26, 31–34] and describes coupled coherent and incoherent motion. Its basic parameters are the \( H_{mn} \)’s, the \( \gamma_{mn} \)’s and the \( \Gamma \). In
terms of them we have shown that while the d.c. conductivity continues to be given by expressions arrived at earlier (see (2.8) and (2.21)), the a.c. conductivity has several new features. The high-temperature approximation is given by (2.7) in connection with (1.2.5) but correction terms appear at non-infinite temperatures as shown by (2.15) together with (1.2.5). An unphysical consequence of the usual [4–6, 13] SLE in $\sigma(\omega)$, via a frequency-independent part is removed by using the generalized [7] SLE. The simple approximations that go to make up the SLE (2.1) result in the appearance of Lorentzians in $\sigma(\omega)$ (2.15). However, the actual details of the dynamics would generally result in non-Lorentzian behaviour (see (3.7, 8)). Indeed our analysis provides an easy access to those details of the dynamics: one may work backwards towards them from the observed $\sigma(\omega)$. It is intended to present an analysis of the experimental data [8, 9, 35] in a future publication.

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