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Exact derivation and solution of the Nakajima-Zwanzig generalized master equation and discussion of approximate treatments for the coupled coherent and incoherent exciton motion

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Starting from the stochastic Liouville equation of the full Haken-Strobl model, describing the coupled coherent and incoherent motion of excitons in molecular crystals, the Nakajima-Zwanzig generalized master equation (GME) for the probability of finding an exciton at a specific lattice site is derived by an exact straightforward evaluation of its memory function. Various recently derived generalized master equations describing the exciton motion are obtained as limiting cases and the Born approximation is discussed. It is shown that, even in the case of nearest-neighbor interaction in the stochastic Liouville equation, in the GME generalized time-dependent transition rates evolve between non-nearest neighbors and that their time behavior shows damped oscillations. Applying the Born approximation to the GME, the range of the generalized transition rates reduces to that of the interaction in the stochastic Liouville equation. Furthermore in this approximation the transition rates show a purely exponential decay with increasing time. Taking into account the interaction with an arbitrary number of neighbors, the mean square displacement of the exciton motion is calculated exactly from the GME. Finally the GME is solved exactly in the general case and several limiting expressions are discussed.

I. INTRODUCTION, STOCHASTIC LIOUVILLE EQUATION, NAKAJIMA-ZWANZIG FORMALISM

The problem of the coupled coherent and incoherent motion of electronic excitations in molecular aggregates has attracted a lot of experimental and theoretical interest[1] in recent years. Theoretical models for the description of exciton motion have been developed mainly along three lines. In the Haken-Strobl model[2-4] of the coupled coherent and incoherent motion of excitons the electronic degrees of freedom are treated quantum mechanically, whereas the influence of the phonons is taken into account in a stochastic manner. From this model a stochastic Liouville equation has been derived, which has been applied to a variety of experimental situations such as diffusion[3,5-8] of excitons, optical absorption[3,9-12] in molecular aggregates, ESR[10,13-15], and NMR,[13,16,17] but also to the description of conductivity[18,19] in organic crystals and of the motion of chemisorbed atoms[20] on a surface. In the second approach to the problem of exciton motion the electronic degrees of freedom as well as those of the phonons are treated quantum mechanically. In such a treatment the phonons may either be considered as a heat bath for the excitons[21,22] or their influence may be taken into account by a canonical transformation.[23-27] In the third method[28-30] the evolution in time of the probability of finding an exciton at a particular lattice site is calculated from a Markoffian master equation.[31-33] As a generalization of this procedure, Kenkre and Knox[34,35] have recently used the non-Markoffian generalized master equation (GME) of Nakajima[36] and Zwanzig[37] for the calculation of the time dependence of the excitonic occupation probability. In contrast to the ordinary master equation, the GME with its non-Markoffian memory function allows one to take care of the coupled coherent and incoherent nature of the exciton motion. Kenkre and Knox have evaluated the kernel of the GME only in lowest (Born) approximation and by this procedure the memory function could be determined from optical absorption and emission spectra.[38]

The relations between the three methods is an interesting problem which merits thorough investigation. Kenkre has treated this question by considering the mean-square displacement calculated in the various models,[34,39,40] and by determining the memory function of the GME from exact solutions of the Schrödinger equation in the case of the completely coherent exciton motion.[41] Furthermore, he has also determined the memory functions of the GME from the solution[3] of the exact stochastic Liouville equation according to Haken, Reineker, and Strobl (HRS)[2-4,15] for a molecular pair[39] and from the solution of a simplified version[42] of that equation for a linear chain of molecules.[41,43] The calculation of the memory function of the GME starting from a microscopic description of the exciton phonon interaction has been carried through by Kenkre and Rahman[44] and by Smith[45] within the Born approximation. Starting from the same microscopic picture, Sokolov and Hizhnyakov[46] have succeeded in obtaining an approximate expression for the memory function; in this calculation no use has been made of the Born approximation. A numerical evaluation of the memory function for the purely coherent exciton motion in one, two, and three dimensions has been carried through by Subrta.[47] Finally, using a method[48] developed recently, which allows the elimination of the projection operator form the kernel of the Nakajima-Zwanzig GME, an exact analytical expression[49] for the memory function of the GME, describing the coherent motion of excitons on an infinite linear chain, was derived for the first time in a straightforward manner.

In this paper we shall show how our straightforward method allows an exact derivation of the GME for the probability of finding an exciton at a specific lattice site, starting from the stochastic Liouville equation for the density operator of the coupled coherent and incoherent exciton motion corresponding to the *full* Haken-Strobl model. To that end in the remainder of this section the Liouville equation of the Haken-Strobl model is represented and the Nakajima-Zwanzig formalism is summarized. In Sec. II the kernel of the GME is calculated, and in Sec. III we represent explicitly the GME together with computer plots of its memory function. In Sec. IV it is shown how from our general equation recent results obtained independently by Kenkre and by us drop out as limiting cases. Starting from the GME, in Sec. V we derive the mean-square displacement for the coupled coherent and incoherent motion, taking into account the interaction with an arbitrary number of neighbors. The exact solution of the GME is represented in Sec. VI and several limiting cases are discussed.

The coupled coherent and incoherent exciton motion is described within the Haken-Strobl model,[2-4] whose Hamiltonian consists of two parts H_0 and $H_1(t)$. The time-independent part H_0 describes the coherent motion of the exciton and is given by

$$H_0=\sum_n \epsilon b_n^\dagger b_n+\sum_{n\neq n'}\sum H_{n-n'}\, b_n^\dagger b_{n'}\,. \qquad (1.1)$$

$b_n^\dagger$ and b_n are creation and annihilation operators for a localized electron hole pair at site n; ϵ is the excitation energy of such a pair and $H_{n-n'}$ the interaction matrix element between sites n and n', which is responsible for the coherent exciton transport. The phase of this coherent, wavelike motion of the excitation energy is disturbed by the phonons. In the Haken-Strobl model the influence of the phonons is treated stochastically, giving rise to a random modulation of the excitation energy and of the interaction matrix elements. These fluctuations are represented by the time dependent part $H_1(t)$ of the Hamiltonian:

$$H_1(t)=\sum_n h_{nn}(t)b_n^\dagger b_n+\sum_{n\neq n'}\sum h_{nn'}(t)b_n^\dagger b_{n'}\,. \qquad (1.2)$$

Mathematically the $h_{nn'}(t)$ are described as δ-correlated Gaussian processes with disappearing mean value and with correlation functions given by

$$\langle h_{nn'}(t)h_{n'n}(t')\rangle=2\gamma_{|n-n'|}\delta(t-t')\,, \qquad (1.3)$$

$$\langle h_{nn'}(t)h_{nn'}(t')\rangle=2\bar\gamma_{n-n'}\delta(t-t') \qquad (1.4)$$

for $n\neq n'$. For $n=n'$ the correlations function is given by

$$\langle h_{nn}(t)h_{nn}(t')\rangle=2\gamma_0\delta(t-t')\,. \qquad (1.5)$$

$\gamma_{|n-n'|}$ and $\bar\gamma_{n-n'}$ describe the strength of the fluctuations. From the total Hamiltonian $H=H_0+H_1(t)$ after averaging over the fluctuations we arrive at the following stochastic Liouville equation (for details see Sec. II A and Appendix A of Ref. 50):

$$\dot{\bar\rho}(t)=\bar L\bar\rho(t)\,. \qquad (1.6)$$

Here we have introduced a modified density operator $\bar\rho$ via

$$\rho(t)=e^{-2\Gamma t}\bar\rho(t)\,, \qquad (1.7)$$

where

$$\Gamma=\sum_m \gamma_m\,. \qquad (1.8)$$

The Liouville operator $\bar L$ is given by [see Eq. (A.19) of Ref. 50]

$$\bar L\bar\rho(t)=-\sum_k \tilde H_k[b_k^\dagger b_k,\bar\rho(t)] +2\sum_k\sum_{k'}\sum_{k''}(\tilde{\bar\gamma}_{k+k''}+\tilde\gamma_{k'-k''})b_k^\dagger b_{k'}\bar\rho(t) \times b_{k''}^\dagger b_{k+k''-k'}\,. \qquad (1.9)$$

$$\bar L=L_1+L_2+L_3\,. \qquad (1.10)$$

The three parts L_1, L_2, and L_3 contain the parameters $\tilde H_k$, $\tilde{\bar\gamma}_k$ and $\tilde\gamma_k$, respectively. $b_k^\dagger$ and b_k are creation and annihilation operators for excitons with wave vector k:

$$b_k=\frac{1}{\sqrt N}\sum_n e^{-ikn}b_n\,. \qquad (1.11)$$

$\tilde H_k$, $\tilde\gamma_k$ and $\tilde{\bar\gamma}_k$ are the Fourier transforms of H_n, $\gamma_{|n|}$, and $\bar\gamma_n$, respectively, and given by [see (2.12)–(2.15) of Ref. 50]

$$\tilde H_k=\sum_m H_m e^{-ikm}\,, \qquad (1.12)$$

$$\tilde\gamma_k=\frac{1}{N}\sum_m \gamma_m e^{-ikm}\,, \qquad (1.13)$$

$$\tilde{\bar\gamma}_k=\frac{1}{N}\sum_m \bar\gamma_m e^{-ikm}\,. \qquad (1.14)$$

We are not interested in the whole information contained in the modified density operator $\bar\rho$, but only in that part describing the probability of finding the exciton at a lattice site n. This information is obtained from $\bar{\rho}$ by the application of a projection operator $\mathcal{P}$ (Refs. 36, 37) projecting out the diagonal part $\bar{\rho}_{nn}$ of $\bar{\rho}$ and is given explicitly in (2.12). The equation of motion for $\mathcal{P}\bar{\rho}$ is [details are given in (2.16)–(2.22) of Ref. 50]

$$\frac{d}{dt}\mathcal{P}\bar{\rho}(t)=\mathcal{P}\bar{L}\mathcal{P}\bar{\rho}(t)+\int_0^t dt' K(t')\mathcal{P}\bar{\rho}(t-t') . \tag{1.15}$$

The kernel $K(t)$ in this expression is defined by

$$K(t)=\mathcal{P}\bar{L}\exp[(1-\mathcal{P})\bar{L}t](1-\mathcal{P})\bar{L}\mathcal{P}. \tag{1.16}$$

In writing (1.15) we have used that an inhomogeneous term in this equation disappears[51–54] (for details see Appendix C of Ref. 50).

II. CALCULATION OF THE KERNEL $K(t)$

A. Transformation of the kernel

In this section the kernel $K(t)$ will be calculated. To that end $K(t)$ of (1.16) will first be expressed by its Laplace transform. After a little algebra $K(t)$ may be written in the following way [see (3.1) of Ref. 50]

$$K(t)=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} dz\, e^{zt}\mathcal{P}\bar{L}\left(\frac{z}{z-(1-\mathcal{P})\bar{L}}-1\right)\mathcal{P}. \tag{2.1}$$

The path of integration has to be chosen parallel to the imaginary axis of the z plane in such a way that all singularities are situated to its left. For $z\to\infty$ the Laplace transform disappears, and therefore the path of integration may be *closed* by a semicircle in the left half-plane. Denoting this closed path by C, from (3.1) we arrive at[55]

$$K(t)=\frac{1}{2\pi i}\int_C dz\, e^{zt}\mathcal{P}\bar{L}\left(\frac{z}{z-(1-\mathcal{P})\bar{L}}-1\right)\mathcal{P}. \tag{2.2}$$

Using the identity

$$\frac{1}{z-\bar{L}+\mathcal{P}\bar{L}}=\frac{1}{z-\bar{L}}-\frac{1}{z-\bar{L}}\mathcal{P}\bar{L}\frac{1}{z-\bar{L}+\mathcal{P}\bar{L}}, \tag{2.3}$$

we obtain

$$\left(\mathcal{P}\frac{1}{z-\bar{L}}\mathcal{P}\right)\left(\mathcal{P}\bar{L}\frac{z}{z-(1-\mathcal{P})\bar{L}}\mathcal{P}\right)=\mathcal{P}\left(\frac{z}{z-\bar{L}}-1\right)\mathcal{P}. \tag{2.4}$$

Dividing by the inverse of the first factor, the kernel $K(t)$ of (2.2) may then be written as [details are given in (3.5)–(3.9) of Ref. 50]

$$K(t)=\frac{1}{2\pi i}\int_C dz\, e^{zt}\left[z-\left(\mathcal{P}\frac{1}{z-\bar{L}}\mathcal{P}\right)^{-1}-\mathcal{P}\bar{L}\right]\mathcal{P}. \tag{2.5}$$

On account of the closed path of integration, the first and third terms in (2.5) disappear and we get

$$K(t)=-\frac{1}{2\pi i}\int_C dz\, e^{zt}\left(\mathcal{P}\frac{1}{z-\bar{L}}\mathcal{P}\right)^{-1}\mathcal{P}. \tag{2.6}$$

The projection operator used in the following is of the form (Ω is an arbitrary operator)

$$\mathcal{P}\Omega=A(B,\Omega)\equiv A\,\mathrm{Tr}(B^\dagger\Omega), \tag{2.7}$$

where the scalar product is defined by the second equality and where on account of $\mathcal{P}^2=\mathcal{P}$ the operators A and B have to satisfy $(B,A)=1$. We insert this form of the projection operator into (2.4) and obtain

$$A\left(B,\frac{1}{z-\bar{L}}A\right)\left(B,\bar{L}\frac{z}{z-(1-\mathcal{P})\bar{L}}A\right)(B,\ldots)$$
$$=A\left(B,\left(\frac{z}{z-\bar{L}}-1\right)A\right)(B,\ldots) . \tag{2.8}$$

Dividing by $(B,\,(z-\bar{L})^{-1}A)$ we get

$$A\left(B,\bar{L}\frac{z}{z-(1-\mathcal{P})\bar{L}}A\right)(B,\ldots)$$
$$=zA(B,\ldots)-\left(B,\frac{1}{z-\bar{L}}A\right)^{-1}A(B,\ldots) . \tag{2.9}$$

From the comparison with (2.4), and after dividing by $(\mathcal{P}(z-\bar{L})^{-1}\mathcal{P})$, we obtain

$$\left(\mathcal{P}\frac{1}{z-\bar{L}}\mathcal{P}\right)^{-1}\mathcal{P}\ldots=\left(B,\frac{1}{z-\bar{L}}A\right)^{-1}A(B,\ldots). \tag{2.10}$$

Equation (2.10) shows that the problem of the calculation of the kernel of the GME has been reduced to that of the determination of a Green's function.

B. Definition of the projection operator

Instead of the stochastic Liouville Eq. (1.6) for the total density operator $\bar{\rho}$ we wish to obtain a GME (1.15), which describes the time evolution of that part of the density operator $\bar{\rho}$, which is diagonal in the site representation. In the following we shall define a projection operator $\mathcal{P}_\kappa$ which projects out this part of the density operator (more exactly its Fourier transform). The diagonal matrix elements of the density operator in the site representation are expressed in the following way by its Fourier transforms:

$$\rho_{nn}=\sum_\kappa e^{i\kappa n}\tilde{\rho}_\kappa , \tag{2.11}$$

where $\tilde{\rho}_\kappa=\sum_k \tilde{\rho}_{k,k-\kappa}$. The projection operator projecting out this component of the density operator is given by

$$\mathcal{P}_\kappa\Omega=(1/N)n_\kappa(n_\kappa,\Omega)\equiv(1/N)n_\kappa\,\mathrm{Tr}(n_\kappa^\dagger\Omega) . \tag{2.12}$$

Here the operators n_κ are defined by

$$n_\kappa = \sum_k n_{k\kappa} \tag{2.13}$$

where $n_{k\kappa} = |k\rangle\langle k-\kappa|$ and $\langle\ |$ and $|\ \rangle$ denote Dirac's bra and ket vectors. From these definitions we immediately derive

$$(n_{k_1\kappa}, n_{k_2\kappa'}) = \delta_{k_1k_2}\delta_{\kappa\kappa'} . \tag{2.14}$$

With this result we easily prove the fundamental property of projection operators $\mathcal{P}_\kappa^2\Omega = \mathcal{P}_\kappa\Omega$. Using this projection operator in (2.10) we have with $A = (1/N)n_\kappa$ and $B = n_\kappa$

$$\left(\mathcal{P}_\kappa \frac{1}{z-\bar{L}}\mathcal{P}_\kappa\right)^{-1}\mathcal{P}_\kappa\Omega = \frac{1}{N}n_\kappa\left(n_\kappa, \frac{1}{z-\bar{L}}\frac{1}{N}n_\kappa\right)^{-1}(n_\kappa, \ldots) . \tag{2.15}$$

C. Calculation of $\left(n_\kappa, \frac{1}{z-\bar{L}}\frac{1}{N}n_\kappa\right)$

The kernel (2.6) is mainly determined by the matrix element in (2.15). Using the definition (2.13) we have

$$\left(n_\kappa, \frac{1}{z-\bar{L}}\frac{1}{N}n_\kappa\right) = \frac{1}{N}\sum_{k_1}\sum_{k_2}\left(n_{k_1\kappa}, \frac{1}{z-\bar{L}}n_{k_2\kappa}\right). \tag{2.16}$$

The decomposition of the Liouville operator $\bar{L} = L_1 + L_2 + L_3$ introduced in (2.10) allows us to write the following identity·

$$\frac{1}{z-\bar{L}} = \frac{1}{z-L_1} + \frac{1}{z-\bar{L}}(L_2+L_3)\frac{1}{z-L_1} . \tag{2.17}$$

Using (2.17) and

$$L_1 n_{k_0,\kappa} = -i(\tilde{H}_{k_0} - \tilde{H}_{k_0-\kappa})n_{k_0,\kappa} , \tag{2.18}$$

$$L_2 n_{k_0,\kappa} = 2\sum_k \bar{\tilde{\gamma}}_{k+k_0-\kappa} n_{k,\kappa} , \tag{2.19}$$

$$L_3 n_{k_0,\kappa} = 2\tilde{\gamma}_\kappa n_\kappa , \tag{2.20}$$

[see also (B.7)–(B.9) of Ref. 50] we obtain the following equation for the matrix elements in (2.16):

$$\sum_{k''}\left(\delta_{k''k} - \frac{2\tilde{\gamma}_\kappa}{z+i(\tilde{H}_k - \tilde{H}_{k-\kappa})} - \frac{2\bar{\tilde{\gamma}}_{k''+k-\kappa}}{z+i(\tilde{H}_k - \tilde{H}_{k-\kappa})}\right) \times \left(n_\kappa, \frac{1}{z-\bar{L}}n_{k''\kappa}\right) = \frac{1}{z+i(\tilde{H}_k - \tilde{H}_{k-\kappa})} . \tag{2.21}$$

[For details of the calculation see Eqs. (3.32)–(3.35) and Appendix B of Ref. 50.] Equation (2.21) represents an inhomogeneous set of algebraic equations for the matrix elements of interest. The equations for different matrix elements are coupled via $\bar{\tilde{\gamma}}_{k''+k-\kappa}$. Inserting (1.14), using the transformation $k \to k + \frac{1}{2}\kappa$, $k'' \to k'' + \frac{1}{2}\kappa$ and applying $(1/N)\sum_k e^{ikn}$, we have from (2.21)

$$f_n - 2\tilde{\gamma}_\kappa N I_n f_0 - \sum_{n'} 2\bar{\gamma}_{n'}(1-\delta_{n'0}) I_{n-n'} f_{-n'} = -I_n . \tag{2.22}$$

Here the abbreviations

$$f_n = -\frac{1}{N}\sum_k e^{ikn}\left(n_\kappa, \frac{1}{z-\bar{L}}|k+\tfrac{1}{2}\kappa\rangle\langle k-\tfrac{1}{2}\kappa|\right) \tag{2.23}$$

and

$$I_n = \frac{1}{N}\sum_k e^{ikn}\frac{1}{z+i(\tilde{H}_{k+\kappa/2} - \tilde{H}_{k-\kappa/2})} \tag{2.24}$$

have been introduced. [Details are given in (3.36)–(3.40) of Ref. 50.] For the calculation of the kernel of the GME we only need

$$-f_0 = \left(n_\kappa, \frac{1}{z-\bar{L}}\frac{1}{N}n_\kappa\right). \tag{2.25}$$

In order to obtain explicit results, we consider nearest-neighbor interaction. In this case (2.22) gives

$$(1 - 2\bar{\gamma}_1 I_{-2})f_{-1} - 2\tilde{\gamma}_\kappa N I_{-1} f_0 - 2\bar{\gamma}_{-1} I_0 f_1 = -I_{-1} , \tag{2.26a}$$

$$-2\bar{\gamma}_1 I_{-1} f_{-1} + (1 - 2\tilde{\gamma}_\kappa N I_0) f_0 - 2\bar{\gamma}_{-1} I_1 f_1 = -I_0 , \tag{2.26b}$$

$$-2\bar{\gamma}_1 I_0 f_{-1} - 2\tilde{\gamma}_\kappa N I_1 f_0 + (1 - 2\bar{\gamma}_{-1} I_2) f_1 = -I_1 . \tag{2.26c}$$

For an infinite chain of molecules and nearest-neighbor interaction (2.24) transforms to

$$I_n = \frac{1}{2\pi}\int_{-\pi}^{\pi} dk \frac{e^{ikn}}{z - i4H_1 \sin k \sin\frac{1}{2}\kappa} . \tag{2.27}$$

Evaluation of this integral in the complex plane results in

$$I_n = \frac{1}{a_\kappa^n}\frac{[z - (z^2 + a_\kappa^2)^{1/2}]^n}{(z^2 + a_\kappa^2)^{1/2}} , \quad n \geq 0 \tag{2.28}$$

with $I_{-n} = (-1)^n I_n$ and $a_\kappa = 4H_1 \sin\frac{1}{2}\kappa$. Assuming still $\bar{\gamma}_1 = \bar{\gamma}_{-1}$, from the solution of (2.26) we obtain

$$-\frac{1}{f_0(\kappa,z)} = \left(n_\kappa, \frac{1}{z-\bar{L}}\frac{1}{N}n_\kappa\right)^{-1} = -2\tilde{\gamma}_\kappa N + z + \frac{(z^2+a_\kappa^2)^{1/2} - z}{1 + (4\bar{\gamma}_1/a_\kappa^2)[(z^2+a_\kappa^2)^{1/2} - z]} . \tag{2.29}$$

With (2.6), (2.15), and (2.29) the kernel of the GME may be written in the following way:

$$K(t)\Omega = \frac{1}{2\pi i}\int_C dz\, e^{zt}\frac{1}{f_0(\kappa,z)}\frac{1}{N}n_\kappa(n_\kappa, \Omega) \tag{2.30}$$

(Ω again being an arbitrary operator), and the retarded term in (1.15) becomes

$$\int_0^t dt' K(t')\mathcal{P}_\kappa\bar{\rho}(t-t') = \frac{1}{2\pi i}\int_0^t dt' \int_C dz\, e^{zt'} \times \frac{1}{f_0(\kappa,z)}\frac{1}{N}n_\kappa\bar{\tilde{\rho}}_\kappa(t-t') , \tag{2.31}$$

where use has been made of (D5) of Ref. 50.

III. GENERALIZED MASTER EQUATION FOR THE COUPLED COHERENT AND INCOHERENT MOTION OF EXCITONS

In order to obtain explicit results for the memory function of the GME, in this section its kernel is represented in a form which easily allows computer evaluation. The first (nonretarded) term of (1.15) may immediately be evaluated with the help of Eqs. (4.1), (4.2), and (D.3) of Ref. 50:

$$\mathcal{P}_\kappa \mathcal{L} \mathcal{P}_\kappa \bar{\rho}(t) = n_\kappa 2\tilde{\gamma}_\kappa \bar{\bar{\rho}} = 2N\tilde{\gamma}_\kappa \mathcal{P}_\kappa \bar{\rho}(t) . \qquad (3.1)$$

In arriving at (3.1) use has been made of (2.18)–(2.20) and of $\sum_k \tilde{H}_k = \sum_k \tilde{H}_{k-\kappa}$. With (2.31), (3.1), and dropping now the operator n_κ occurring in each term, from (1.15) we arrive

$$\frac{d}{dt}\bar{\bar{\rho}}_\kappa(t) = 2N\tilde{\gamma}_\kappa \bar{\bar{\rho}}_\kappa(t) + \frac{1}{2\pi i}\int_0^t dt' \int_C dz\, e^{zt'} \frac{1}{f_0(\kappa,z)} \bar{\bar{\rho}}_\kappa(t-t') . \qquad (3.2)$$

Using (1.7), this equation is obtained in a form which will be the starting point for the calculation of the mean-square displacement of the coupled coherent and incoherent exciton motion in Sec. IV:

$$\frac{d}{dt}\tilde{\rho}_\kappa(t) = -2(\Gamma - N\tilde{\gamma}_\kappa)\tilde{\rho}_\kappa(t) + \frac{1}{2\pi i}\int_0^t dt' \int_C dz\, e^{(z-2\Gamma)t'} \times \frac{1}{f_0(\kappa,z)}\tilde{\rho}_\kappa(t-t') . \qquad (3.3)$$

Transforming now to the site representation, this equation reads:

$$\frac{d}{dt}\rho_n(t) = -2\Gamma\rho_n(t) + \sum_{n'} 2\gamma_{n-n'}\rho_{n'}(t) + \sum_{n'} \int_0^t dt' \int_C \frac{dz}{2\pi i} \exp[(z-2\Gamma)t'] \frac{1}{N}\sum_\kappa \exp[i\kappa(n-n')] \times \left[2N\tilde{\gamma}_\kappa - z - \frac{(z^2+a_k^2)^{1/2} - z}{1 + (4\bar{\gamma}_1/a_k^2)[(z^2+a_\kappa^2)^{1/2} - z]}\right]\rho_{n'}(t-t') , \qquad (3.4)$$

where (1.13) and (2.11) with $\rho_{nn}(t) \equiv \rho_n(t)$ have been used. As described in Sec. II A the path of integration C in the z plane runs parallel to the imaginary axis and is closed in the left half-plane including all singularities of the integrand. On account of the analyticity with respect to z the contributions of the first and second terms in the integrand disappear and we obtain:

$$\frac{d}{dt}\rho_n(t) = -2\Gamma\rho_n(t) + \sum_{n'} 2\gamma_{n-n'}\rho_{n'}(t) + \sum_{n'} \int_0^t dt'\, e^{-2\Gamma t'} K_{n-n'}(t')\rho_{n'}(t-t') . \qquad (3.5)$$

For a linear chain of molecules of infinite length we have,

$$K_{n-n'}(t) = \int_{-\pi}^{\pi} \frac{d\kappa}{2\pi} \exp[i\kappa(n-n')]\tilde{K}_\kappa(t) , \qquad (3.6)$$

where

$$\tilde{K}_\kappa(t) = -\int_C \frac{dz}{2\pi i}\, e^{zt} \frac{a_\kappa^2}{(z^2+a_\kappa^2)^{1/2} + z + 4\bar{\gamma}_1} . \qquad (3.7)$$

For the evaluation of the integral in the z plane we introduce a new variable

$$w = |a_\kappa|^{-1}[z + (z^2+a_\kappa^2)^{1/2}] , \qquad (3.8)$$

and from (3.7) we get

$$\tilde{K}_\kappa(t) = -\frac{a_\kappa^2}{2}\int_{C'} \frac{dw}{2\pi i} \exp[\tfrac{1}{2}|a_\kappa| t(w - 1/w)] \times \frac{1 + 1/w^2}{w + 4\bar{\gamma}_1/|a_\kappa|} , \qquad (3.9)$$

where the path of integration C' is *closed* in the w plane, encircles the origin in the positive sense and includes all singularities. The exponential in (3.9) is the generating function of the Bessel functions of integer order.[57] Inserting this expansion into (3.9) and interchanging summation and integration, we arrive at [see also Eq. (4.12) of Ref. 50]

$$\tilde{K}_\kappa(t) = -\frac{|a_\kappa|^2}{2}\sum_{n=-\infty}^{\infty} [J_n(|a_\kappa| t) + J_{n+2}(|a_\kappa| t)] \times \int_{C'} \frac{dw}{2\pi i} \frac{w^n}{w + 4\bar{\gamma}_1/|a_\kappa|} . \qquad (3.10)$$

The evaluation of the integral gives

$$\int_{C'} \frac{dw}{2\pi i} \frac{w^n}{w + 4\bar{\gamma}_1/|a_\kappa|} = \begin{cases} (-4\bar{\gamma}_1/|a_\kappa|)^n, & n \geq 0 \\ 0, & n < 0 . \end{cases} \qquad (3.11)$$

Using functional relations for Bessel functions[57] the Fourier transform $\tilde{K}_\kappa(t)$ (3.10) of the kernel becomes

$$\tilde{K}_\kappa(t)=\frac{|a_\kappa|^2}{4\bar{\gamma}_1 t}\sum_{n=1}^{\infty} nJ_n(|a_\kappa|t)\left(-\frac{4\bar{\gamma}_1}{|a_\kappa|}\right)^n . \tag{3.12}$$

Expanding the Bessel functions into a power series[57] and introducing dimensionless variables

$$\tau=2H_1 t,\quad \bar{\gamma}=\bar{\gamma}_1/H_1 \tag{3.13}$$

from (3.12) we have [see also Eqs. (4.15) and (4.17) of Ref. 50]

$$\tilde{K}'_\kappa(\tau)=\tilde{K}_\kappa\left(\frac{\tau}{2H_1}\right)=-8H_1^2\sin^2\frac{\kappa}{2}\sum_{n=1}^{\infty} n(-\bar{\gamma}\tau)^{n-1}\times\sum_{k=0}^{\infty}\frac{(-1)^k\tau^{2k}\sin^{2k}\frac{1}{2}\kappa}{k!(n+k)!} . \tag{3.14}$$

With the help of

$$\int_0^1 du(1-u)^{n-1}u^k=\frac{(n-1)!k!}{(n+k)!} , \tag{3.15}$$

expression (3.14) may be written in the following way:

$$\tilde{K}'_\kappa(\tau)=-8H_1^2\sin^2\frac{\kappa}{2}\int_0^1 du\sum_{n=0}^{\infty}\sum_{k=0}^{\infty}\frac{n(-\bar{\gamma}\tau)^{n-1}}{(n-1)!}\times(1-u)^{n-1}u^k\frac{(-1)^k\tau^{2k}\sin^{2k}\frac{1}{2}\kappa}{k!k!} . \tag{3.16}$$

The summation of the two series in (3.16) may be carried through explicitly:

$$J_0(2\tau\sqrt{u}\sin\tfrac{1}{2}\kappa)=\sum_{k=0}^{\infty}\frac{(-1)^k\tau^{2k}u^k\sin^{2k}\frac{1}{2}\kappa}{k!k!} , \tag{3.17}$$

$$(1+\alpha)e^{\alpha}=\sum_{n=1}^{\infty}\frac{n}{(n-1)!}\alpha^{n-1} . \tag{3.18}$$

The kernel of the GME in the site representation is given by (3.6) and we thus arrive at

$$K'_m(\tau)=K_m\left(\frac{\tau}{2H_1}\right)=-4H_1^2\int_0^1 dx\, x[1-\bar{\gamma}\tau(1-x^2)]\exp[-\bar{\gamma}\tau(1-x^2)]\int_{-\pi}^{\pi}\frac{d\kappa}{2\pi}(2e^{i\kappa m}-e^{i\kappa(m+1)}-e^{-i\kappa(m-1)})J_0(2\tau x\sin\tfrac{1}{2}\kappa) , \tag{3.19}$$

where $x^2=u$ has been introduced as a new variable. Using the following relation between Bessel functions,[57]

$$J_n^2(t')=\int_{-\pi}^{\pi}\frac{d\kappa}{2\pi}e^{i\kappa n}J_0(2t'\sin\tfrac{1}{2}\kappa) , \tag{3.20}$$

we finally get the previously reported result[58]

$$K'_m(\tau)=4H_1^2\int_0^1 dx\, x[1-\bar{\gamma}\tau(1-x^2)]\exp[-\bar{\gamma}\tau(1-x^2)]\times[J_{m+1}^2(\tau x)+J_{m-1}^2(\tau x)-2J_m^2(\tau x)] . \tag{3.21}$$

In Fig. 1(a) we have pictured

$$\bar{K}_m(\tau)=K'_m(\tau)/4H_1^2;\quad m=1,\ldots,10 , \tag{3.22}$$

as a function of τ for $\bar{\gamma}=\bar{\gamma}_1/H_1=0$, i.e., for the completely coherent case. For $\tau=0$ only $\bar{K}_1(\tau)$, describing transitions between nearest neighbors, is different from zero. The other K_m's, describing transitions between neighbors a larger distance apart, are zero at the initial time. With increasing time all transition rates show oscillations with decreasing amplitude. This case of $\bar{\gamma}_1=0$ has also been discussed by Kenkre,[41] who especially stresses that long distance generalized transfer rates evolve despite the fact that the Liouville equation contains only nearest-neighbor matrix elements. These nonlocal generalized transfer rates obviously have their origin in the elimination of the nondiagonal part of the density operator, which describes phase relations between different lattice sites. These phase relations are naturally most important in the case of the coherent, wavelike motion of the exciton. In Figs. 1(b) and 1(c) the same quantities are represented for $\bar{\gamma}=0.5$ and $\bar{\gamma}=2.0$. The essential points are that the initial amplitude of $\bar{K}_1(\tau)$ now drops more rapidly and that the oscillations decrease rather rapidly as well with increasing time as with increasing values of m. In Fig. 2 the time behavior of $\bar{K}_1(\tau)$ is shown for various values of $\bar{\gamma}$; the curves numbered from 1 to 10 correspond to $\bar{\gamma}$ values of 0, 0.1, 0.5, 1, 2, 5, 10, 20, 50, and 100. This figure shows very distinctly the rapid decay of $\bar{K}_1(\tau)$ with increasing time, when $\bar{\gamma}$ increases.

In the case of single crystals of anthracene we have $\bar{\gamma}\approx 0.01,\ldots,0.1$ even at room temperature.[3] Therefore the real situation is described approximately by Fig. 1(a). However, it is very important to remember that on account of (1.7) the kernel of the GME, i.e., the memory function, is given by $e^{-2\Gamma t}K_m(t)$. In this expression $\Gamma=\gamma_0+2\gamma_1$ is strongly temperature dependent[3] and at room temperature because of $\gamma_0\gg\gamma_1$ much larger than $\gamma_1\approx\bar{\gamma}_1$. For this reason, at room temperature the total memory function decays rapidly.

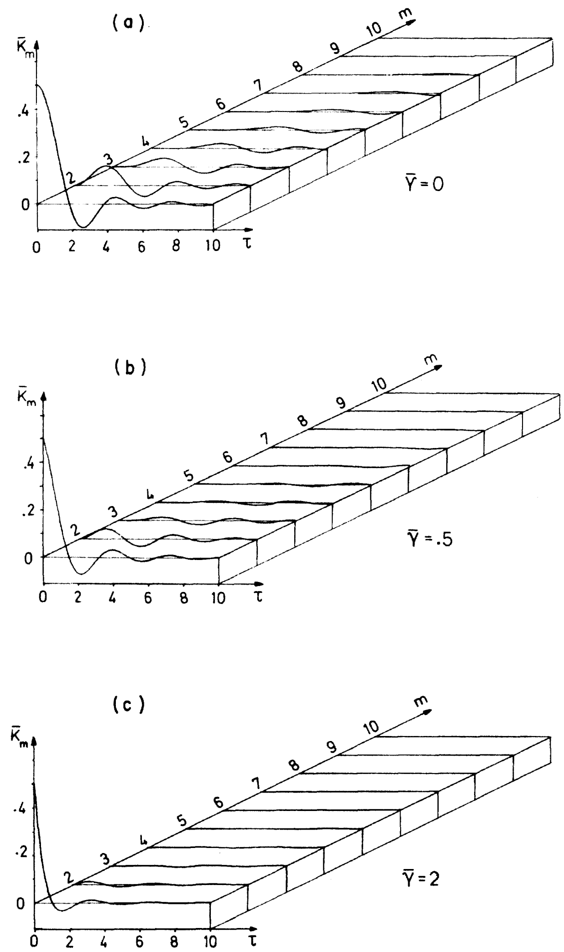

FIG. 1. Generalized transition rates $\bar{K}_m(\tau)$ according to (3.22) for $m=1, \ldots, 10$ and $\bar{\gamma}=0.0$ (a), $\bar{\gamma}=0.5$ (b), and $\bar{\gamma}=2.0$ (c).

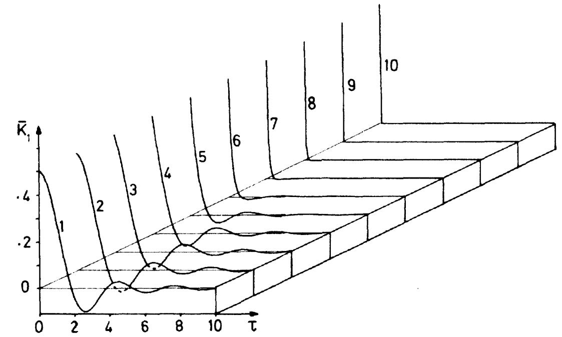

FIG. 2. Generalized transition rates $\bar{K}_1(\tau)$ according to (3.22). The numbering of 1, ..., 10 of the curves corresponds to $\bar{\gamma}=0$, 0.1, 0.5, 1, 2, 5, 10, 20, 50, and 100.

IV. INVESTIGATION OF LIMITING CASES

Starting from expressions (3.5) and (3.21) for the GME, in this section the limiting cases of the purely incoherent, the purely coherent, and the quasi-incoherent exciton motion are considered. Furthermore, we specialize our result to the case $\bar{\gamma}_1=0$ and derive the Born approximation of the GME. It is shown that the generalized master equations obtained recently for a part of these situations by Kenkre[41-43] and by Kühne and Reineker[7,49,59] are included as special cases in the GME of this paper.

A. Purely incoherent exciton motion

In this case $H_{n-n'}=0$. From (3.21) it is seen that $K'_m(\tau)=0$. (3.5) is then given by

$$\dot{\rho}_n(t) = -2\Gamma\rho_n(t) + \sum_{n'} 2\gamma_{n-n'}\rho_{n'}(t)\,. \tag{4.1}$$

With the definition of Γ from (1.8), the GME reduces to an ordinary master equation with hopping rates $2\gamma_{n-n'}$ between molecules a distance $n-n'$ apart:

$$\dot{\rho}_n(t) = \sum_{n'(\neq n)} 2\gamma_{n-n'}[\rho_{n'}(t) - \rho_n(t)]\,. \tag{4.2}$$

This equation is identical with the incoherent limit of the stochastic Liouville equation of HRS.[2-4,7]

B. Purely coherent exciton motion

In the limit of $\gamma_{n-n'}=\bar{\gamma}_{n-n'}=\Gamma=0$ the kernel (3.21) of the GME becomes $(\tau x = x')$

$$K'_m(\tau) = \frac{4H_1^2}{\tau^2}\int_0^\tau dx'\,x'[J_{m+1}^2(x') + J_{m-1}^2(x') - 2J_m^2(x')]\,. \tag{4.3}$$

Using a series representation for products of Bessel functions[57] from (4.3) we arrive at

$$K'_m(\tau) = \frac{4H_1^2}{\tau}\frac{d}{d\tau}J_m^2(\tau)\,. \tag{4.4}$$

[Details of the calculation are given in (5.3)–(5.7) of Ref. 50.] In complete coincidence with Ref. 49 we obtain for the GME

$$\frac{d}{dt}\rho_n(t) = \sum_{n'}\int_0^t dt'\left(\frac{1}{t'}\frac{d}{dt'}J_{n-n'}^2(2H_1t')\right) \times \rho_{n'}(t-t')\,. \tag{4.5}$$

It may be shown that the memory function of Kenkre[42] may also be written in this form.

C. Quasi-incoherent exciton motion

Using (3.21), the last term of the GME (4.5) is written

$$A_{nn'}(t) = \int_0^t dt'\, e^{-2\Gamma t'} K_{n-n'}(t')\rho_{n'}(t-t')$$
$$= \int_0^t dt'\, e^{-2\Gamma t'} 4H_1^2 \int_0^1 dx\, x[1 - 2\bar{\gamma}_1 t'(1-x^2)]\exp[-2\bar{\gamma}_1 t'(1-x^2)]$$
$$\times [J^2_{n-n'+1}(2H_1 t'x) + J^2_{n-n'-1}(2H_1 t'x) - 2J^2_{n-n'}(2H_1 t'x)]\rho_{n'}(t-t') . \quad (4.6)$$

In the quasi-incoherent case $\Gamma \gg H_1$, and $\exp(-2\Gamma t')$ decays rapidly with time as compared to the changes of the Bessel functions. Therefore the main contribution of the t' integral stems from $t' \approx 0$. For this reason we evaluate the Bessel functions and $\rho_{n'}$ at $t'=0$ and let the upper limit of the t' integral approach infinity. The evaluation of the integral and of the Bessel function results in [see also Eq. (5.11) of Ref. 50]

$$A_{nn'}(t) = (\delta_{n-n'+1,0} + \delta_{n-n'-1,0} - 2\delta_{n-n',0}) \times \rho_{n'}(t)[H_1^2/(\Gamma + \bar{\gamma}_1)] . \quad (4.7)$$

Taking into account nearest-neighbor interaction also in the incoherent terms, the GME (3.5) becomes

$$\frac{d}{dt}\rho_n(t) = [2\gamma_1 + H_1^2/(\Gamma+\bar{\gamma}_1)](\rho_{n+1} + \rho_{n-1} - 2\rho_n) . \quad (4.8)$$

The comparison with (5.2) shows that in this case the influence of the coherent interaction merely leads to a modification of the incoherent hopping rate[3,7,8].

D. Case of $\bar{\gamma}=0$

Using $\bar{\gamma}=0$ in (3.21), we see that $K'_m(\tau)$ reduces to the expression (4.3) of the purely coherent exciton motion. (However, now $\Gamma \neq 0$.) Using (4.4) and (3.13), from (3.5) we obtain

$$\frac{d}{dt}\rho_n(t) = -2\Gamma\rho_n(t) + \sum_{n'} 2\gamma_{n-n'}\rho_{n'}(t) + \sum_{n'} \int_0^t dt'\, e^{-2\Gamma t'}\left(\frac{1}{t'}\frac{d}{dt'}J^2_{n-n'}(2H_1 t')\right) \times \rho_{n'}(t-t') . \quad (4.9)$$

This result has been achieved recently by Kenkre.[42] As compared to the completely coherent case of Sec. IV B, all memory functions are multiplied by the same damping factor $\exp(-2\Gamma t')$.

E. Derivation of the GME in the Born approximation

The derivation of the GME in the Born approximation is instructive, because this approximation has been used by Kenkre and Knox[35] in order to determine the kernel of the generalized master equation from optical spectra, generalizing in this way the Markoffian result of Förster,[28] and because Silbey[1] and Kenkre[41] have commented on its inapplicability for the case of highly coherent motion.

For the application of this approximation it is convenient to start from (1.15) and (1.16).[59] In the following calculations we again use (1.10) and $\mathcal{P} = \mathcal{P}_\kappa$ from (2.12). The first (nonretarded) term is given in (3.1). After some algebra [for details see (5.15)–(5.19) and Appendices B and D of Ref. 50] we get

$$\frac{d}{dt}\mathcal{P}_\kappa\bar{\rho}(t) = 2N\tilde{\gamma}_\kappa\mathcal{P}_\kappa\bar{\rho}(t) + \int_0^t dt'\mathcal{P}_\kappa L_1 \exp\{[(1-\mathcal{P}_\kappa)L_1 + L_2 + L_3]t'\}L_1\mathcal{P}_\kappa\bar{\rho}(t-t') . \quad (4.10)$$

Up to this point the calculations are exact. The Born approximation now consists in neglecting the term $(1-\mathcal{P}_\kappa)L_1$ in the exponent, stemming from the coherent interaction.

We now use the explicit form (2.12) of the projection operator and drop the factor n_κ, common to all terms:

$$\frac{d}{dt}\bar{\bar{\rho}}_\kappa = 2N\tilde{\gamma}_\kappa\bar{\bar{\rho}}_\kappa + N^{-1}\int_0^t dt'(n_\kappa, L_1 e^{(L_2+L_3)t'}L_1 n_\kappa) \times\bar{\bar{\rho}}_\kappa(t-t') . \quad (4.11)$$

The scalar product in (4.11) may be written as follows:

$$S = (n_\kappa, L_1 e^{(L_2+L_3)t'}L_1 n_\kappa)$$
$$= -\sum_k\sum_{k'} (\tilde{H}_k - \tilde{H}_{k-\kappa})(\tilde{H}_{k'} - \tilde{H}_{k'-\kappa}) \times (n_{k'\kappa}, e^{L_2 t'} n_{k\kappa}) . \quad (4.12)$$

Here we have used $\sum_k(\tilde{H}_k - \tilde{H}_{k-\kappa}) = 0$.

Transforming to the site representation, with the help of (1.12), (1.13), and (2.11) we have

$$\frac{d}{dt}\bar{\rho}_n(t)=\sum_{n'} 2\gamma_{n-n'}\bar{\rho}_{n'}(t)+4\sum_{\kappa}\sum_{m}\sum_{m'}\sum_{m''} N^{-2}\int_0^t dt' \exp[i\kappa(n-m'')]H_m H_{m'} \sin\tfrac{1}{2}\kappa m' \sin\tfrac{1}{2}\kappa m$$
$$\times\sum_{k}\sum_{k'} e^{i(\kappa/2)m} e^{i(\kappa/2)m'} e^{-ik'm'} e^{-ikm}(n_{k'\kappa}, e^{L_2 t} n_{k\kappa})\bar{\rho}_{m''}(t-t') . \qquad (4.13)$$

We denote the last line by $A_{m',-m}$, and from the differential equation for this expression we get [details are given in (5.26)–(5.29) of Ref. 50]

$$A_{m',-m}(t)=\alpha\, e^{2\bar{\gamma}_m t}-\beta\, e^{-2\bar{\gamma}_m t}, \qquad (4.14)$$

with $\alpha=\frac{1}{2}N(\delta_{m',m}+\delta_{m',-m})$ and $\beta=\frac{1}{2}N(\delta_{m',m}-\delta_{m',-m})$. Inserting now (4.14) into (4.13), evaluating the Kronecker symbols and using once more the inversion symmetry, i.e., $H_m=H_{-m}$, with the help of (1.7) we finally get

$$\frac{d}{dt}\rho_n(t)=\sum_m 2\gamma_m[\rho_{n+m}(t)-\rho_n(t)] + \sum_m\int_0^t dt'\, 2H_m^2 \exp[-2(\Gamma+\bar{\gamma}_m)t'] \times[\rho_{n+m}(t-t')-\rho_n(t-t')] . \qquad (4.15)$$

The comparison of this result with the exact evaluation in Sec. III and with the purely coherent motion discussed in Sec. IV B and in Refs. 41 and 49 reveals differences in two points: first, in the case of nearest-neighbor interaction, $H_m=H_1(\delta_{m,1}+\delta_{m,-1})$, the kernel of (4.15) gives interaction only between nearest neighbors, whereas in the two other cases mentioned above an interaction also between non-nearest neighbors exists. This point has also been stressed by Kenkre.[41] Second, in the exact evaluation and in the limit of the purely coherent motion, the kernels show an oscillatory behavior in time, whereas the kernel in (4.15) decays exponentially. The Markoffian limit, i.e., the quasi-incoherent motion, is obtained from (4.15), if the exponential decays so rapidly that the essential contribution to the integral in (4.15) is obtained for $t'\approx 0$. Then $\rho_{n+m}(t-t')-\rho_n(t-t')\approx\rho_{n+m}(t)-\rho_n(t)$, and the upper limit in the integral may be replaced by infinity. In this way one arrives at the ordinary master equation (4.8).

V. MEAN-SQUARE DISPLACEMENT OF THE COUPLED COHERENT AND INCOHERENT EXCITON MOTION

The calculation of the mean-square displacement of the exciton motion may be executed, taking not only into account the interaction with nearest, but with an arbitrary number of neighbors, without explicitly solving the equation of motion (3.3) for $\tilde{\rho}_\kappa(t)$ and (2.22) for $f_n(\kappa,z)$.[60] Using (2.11) we may express the Fourier transform $\tilde{\rho}_\kappa(t)$ by the diagonal elements $\rho_n(t)$ of the density operator, representing the probability of finding the exciton at time t at site n:

$$\tilde{\rho}_\kappa=\frac{1}{N}\sum_n e^{i\kappa n}\rho_n(t). \qquad (5.1)$$

From this expression we immediately verify that the mean-square displacement may be written in the following manner:

$$\langle n^2\rangle=\sum_n n^2\rho_n(t)=-N\frac{\partial^2}{\partial\kappa^2}\tilde{\rho}_\kappa\bigg|_{\kappa=0}. \qquad (5.2)$$

Differentiating (3.3) twice with respect to κ, we obtain

$$\frac{\partial}{\partial t}\frac{\partial^2\tilde{\rho}_\kappa}{\partial\kappa^2}=-2\Gamma\frac{\partial^2\tilde{\rho}_\kappa}{\partial\kappa^2}+2N\left(\frac{\partial^2\tilde{\gamma}_\kappa}{\partial\kappa^2}\right)\tilde{\rho}_\kappa+4N\left(\frac{\partial\tilde{\gamma}_\kappa}{\partial\kappa}\right)\left(\frac{\partial\tilde{\rho}_\kappa}{\partial\kappa}\right)+2N\tilde{\gamma}_\kappa\left(\frac{\partial^2\tilde{\rho}_\kappa}{\partial\kappa^2}\right)$$
$$+\int_0^t dt'\int_C\frac{dz}{2\pi i}\exp[(z-2\Gamma)t']$$
$$\times\left[\frac{2}{[f_0(\kappa,z)]^3}\left(\frac{\partial}{\partial\kappa}f_0(\kappa,z)\right)^2\tilde{\rho}_\kappa(t-t')-\frac{1}{[f_0(\kappa,z)]^2}\left(\frac{\partial^2}{\partial\kappa^2}f_0(\kappa,z)\right)\tilde{\rho}_\kappa(t-t')\right.$$
$$\left.-\frac{2}{[f_0(\kappa,z)]^2}\left(\frac{\partial}{\partial\kappa}f_0(\kappa,z)\right)\frac{\partial\tilde{\rho}_\kappa(t-t')}{\partial\kappa}+\frac{1}{f_0(\kappa,z)}\frac{\partial^2}{\partial\kappa^2}\tilde{\rho}_\kappa(t-t')\right]. \qquad (5.3)$$

In order to obtain the mean-square displacement, this expression has to be evaluated for $\kappa=0$.

From (1.13) and (1.8) and using the initial conditions $\rho_n(t=0)=\delta_{n0}$ it is obvious that the first and the fourth terms on the right-hand side of (5.3) cancel and that the third term disappears. The remaining terms in (5.3) have to be determined from Eq. (2.22) for $f_n(\kappa, z)$. For $\kappa = 0$ we get after some calculations (for details see Sec. VI of Ref. 50).

$$f_n(0,z) = \frac{\delta_{n0}}{2\Gamma - z}\ , \tag{5.4a}$$

$$\left.\frac{\partial f_n(\kappa,z)}{\partial\kappa}\right|_{\kappa=0} = -\frac{nH_n}{z(2\Gamma - z)}\frac{z}{z+2\bar{\gamma}_n}\ , \tag{5.4b}$$

$$\left.\frac{\partial^2 f_0(\kappa,z)}{\partial\kappa^2}\right|_{\kappa=0} = \frac{1}{(z-2\Gamma)^2}\sum_m\left(\frac{2m^2H_m^2}{z+2\bar{\gamma}_m} + 2\bar{\gamma}_m m^2\right). \tag{5.4c}$$

Inserting these results into (5.3) we get

$$\frac{\partial}{\partial t}\left.\frac{\partial^2\tilde{\rho}_\kappa(t)}{\partial\kappa^2}\right|_{\kappa=0} = -2N^{-1}\sum_m m^2\gamma_m + \int_0^t dt' \int_C \frac{dz}{2\pi i}\, e^{(z-2\Gamma)t'}\left(-(2\Gamma - z)^2 N^{-1}\frac{\partial^2}{\partial\kappa^2} f_0(\kappa,z)\big|_{\kappa=0} + (2\Gamma - z)\frac{\partial^2}{\partial\kappa^2}\tilde{\rho}_\kappa(t-t')\Big|_{\kappa=0}\right). \tag{5.5}$$

The second term in the large parentheses in (5.5) is analytic and gives no contribution when calculating the z integral. For the same reasons the z integral over the second term in (5.4c) disappears, and we have

$$\frac{\partial}{\partial t}\left.\frac{\partial^2\tilde{\rho}_\kappa(t)}{\partial\kappa}\right|_{\kappa=0} = -2N^{-1}\sum_m m^2\gamma_m - N^{-1}\int_0^t dt'\, e^{-2\Gamma t'} \times \int_C \frac{dz}{2\pi i}\, e^{zt'}\sum_m \frac{2m^2H_m^2}{z+2\gamma_m}\,. \tag{5.6}$$

Integrating with respect to t' and t and using the initial condition $\langle n^2\rangle|_{t=0} = 0$ we have [see also (6.11) of Ref. 50]

$$\langle n^2\rangle = \sum_m m^2\left(2\gamma_m + \frac{H_m^2}{\Gamma+\bar{\gamma}_m}\right)t + \sum_m \frac{2m^2H_m^2}{(2\Gamma+2\bar{\gamma}_m)^2}\{\exp[-(2\Gamma+2\bar{\gamma}_m)t] - 1\}. \tag{5.7}$$

This result coincides with that derived directly from the Liouville equation.[6] The comparison of (5.7) with (3.21) shows that the detailed, oscillating time structure stemming from the Bessel functions is completely lost, when considering the mean-square displacement. In the case of nearest-neighbor interaction, besides the term linear in t we have only a single exponential term. For interaction with an arbitrary number of neighbors, this exponential term is replaced by a sum of exponentials with different amplitudes and decay rates. The prefactor of the term linear in t is just the diffusion constant for excitons.[3,6-8] In diffusion experiment[61] only this combination of the model parameters is measured and no information on γ_m, $\bar{\gamma}_m$, Γ, and H_m separately can be obtained. Therefore, from diffusion experiments alone, we cannot decide whether $\Gamma < H_m$ or $\Gamma > H_m$, i.e., whether the exciton motion is coherent or incoherent. The additional information necessary for answering this question may, however, be derived[3] from optical absorption experiments.[62]

VI. SOLUTIONS OF THE MASTER EQUATION

A. General solution of the master equation

In this subsection we present the solution of our GME (3.2). Various limiting cases will be considered in Secs. VI B–VI D. Using (2.29), from (3.2) we obtain

$$\frac{d}{dt}\bar{\bar{\rho}}_\kappa(t) = 2N\tilde{\gamma}_\kappa\bar{\bar{\rho}}_\kappa(t) - \int_0^t dt'\int_C\frac{dz}{2\pi i}\, e^{zt'}\left(-2N\tilde{\gamma}_\kappa + z + \frac{(z^2+a_\kappa^2)^{1/2} - z}{1 + (4\bar{\gamma}_1/a_\kappa^2)[(z^2+a_\kappa^2)^{1/2} - z]}\right)\bar{\bar{\rho}}_\kappa(t-t')\,. \tag{6.1}$$

The integral in the z plane of the first and second terms in the large parentheses disappears on account of their analytic nature. The remaining integral may be reduced to a Laplace integral, because its contribution along the semicircle in the left half-plane at infinity vanishes. Using the convolution theorem, the Laplace transform of (6.1) may easily be calculated and solving for $\bar{\bar{\rho}}_\kappa(z)$, we have[63]

$$\bar{\bar{\rho}}_\kappa(z) = \frac{\bar{\bar{\rho}}_\kappa(t=0)}{z - 2N\tilde{\gamma}_\kappa + [(z^2+a_k^2)^{1/2} - z]/\{1 + (4\bar{\gamma}_1/a_\kappa^2)[(z^2+a_\kappa^2)^{1/2} - z]\}}\ . \tag{6.2}$$

The time dependence of $\bar{\bar{\rho}}_\kappa$ is then given by its Laplace transform. The path of integration may naturally again be closed by a semicircle in the left half-plane. In analogy to (3.8) we introduce a new variable (with a slight modification[64]) $\bar{w} = z + (z^2 + a_\kappa^2)^{1/2}$, and $z = \frac{1}{2}(\bar{w} - a_\kappa^2/\bar{w})$ and arrive at

$$\bar{\tilde{\rho}}_\kappa(t) = \int_{C'} \frac{d\bar{w}}{2\pi i} \exp\left[\frac{1}{2}\left(\bar{w} - \frac{a_\kappa^2}{\bar{w}}\right)t\right]\left(1 + \frac{a_\kappa^2}{\bar{w}^2}\right)\frac{\bar{w}(\bar{w}+4\bar{\gamma}_1)}{\bar{w}^3 + \bar{w}^2(4\bar{\gamma}_1 - 4N\tilde{\gamma}_\kappa) + \bar{w}(a_\kappa^2 - 16N\tilde{\gamma}_\kappa\bar{\gamma}_1) - 4\bar{\gamma}_1 a_\kappa^2}\,\bar{\tilde{\rho}}_\kappa(t=0)\,. \tag{6.3}$$

The path of integration C' is essentially the same as described after (3.9). We expand the third factor into partial fractions and introduce $A_i\,(i = 1, 2, 3)$ by

$$A_1 = [\bar{w}_1(\bar{w}_1 + 4\bar{\gamma}_1)]/[(\bar{w}_1 - \bar{w}_2)(\bar{w}_1 - \bar{w}_3)] \tag{6.4}$$

and cyclic permutation. The $\bar{w}_i$'s are the zeros of the denominator of (6.3). Using still the series expansion of the exponential of (6.3), this equation may be written as

$$\bar{\tilde{\rho}}_\kappa(t) = \sum_{i=1}^{3}\sum_m\sum_k \left(\frac{(\frac{1}{2}t)^{m+k}(-\frac{1}{2}a_\kappa^2 t)^k}{(m+k)!k!} + \frac{(\frac{1}{2}t)^{m+2+k}(-\frac{1}{2}a_\kappa^2 t)^k a_\kappa^2}{(m+2+k)!k!}\right)A_i \times \int_C \frac{d\bar{w}}{2\pi i}\frac{\bar{w}^m}{\bar{w} - \bar{w}_i}\tilde{\rho}_\kappa(t=0)\,. \tag{6.5}$$

With the help of (3.11) we obtain

$$\bar{\tilde{\rho}}_\kappa(t) = \tilde{\rho}_\kappa(t=0)\sum_{i=1}^{3}\sum_{m=0}^{\infty}\sum_k A_i(\tfrac{1}{2}\bar{w}_i t)^m \times \left[\frac{(\frac{1}{2}|a_\kappa|t)^{2k}(-1)^k}{(m+k)!k!} + \frac{(\frac{1}{2}|a_\kappa|t)^{2k+2}(-1)^k}{(m+k+2)!k!}\right] \tag{6.6}$$

and from this expression we immediately arrive at

$$\bar{\tilde{\rho}}_\kappa(t) = \bar{\tilde{\rho}}_\kappa(t=0)\sum_{i=1}^{3}\sum_{m=0}^{\infty}\sum_k A_i(\tfrac{1}{2}\bar{w}_i t)^{m-1} \times (\tfrac{1}{2}a_\kappa t)^{2k}(-1)^k\frac{m}{(m+k)!k!}\,. \tag{6.7}$$

The following calculations may be carried through in complete analogy to those leading to (3.19), and using again (3.15), (3.17), and (3.18) we arrive at

$$\tilde{\rho}_\kappa(t) = \tilde{\rho}_\kappa(t=0) \times \sum_{i=1}^{3}\int_0^1 du A_i\left(\frac{\partial}{\partial u}(u-1)\exp[\tfrac{1}{2}\bar{w}_i t(1-u)]\right) \times J_0(\sqrt{u}|a_\kappa|t)\,. \tag{6.8}$$

In the site representation and using (1.7), our final result is

$$\rho_n(t) = \sum_\kappa \exp(i\kappa n - 2\Gamma t)\tilde{\rho}_\kappa(t=0) \times \sum_{i=1}^{3}\int_0^t du A_i\left(\frac{\partial}{\partial u}(u-1)\exp[\tfrac{1}{2}\bar{w}_i t(1-u)]\right) \times J_0(\sqrt{u}|a_\kappa|t)\,. \tag{6.9}$$

B. Solution in the purely coherent case

In this limiting case $\bar{\gamma}_1 = \tilde{\gamma}_\kappa = 0$ and the zeros of the denominator of (6.3) are given by $\bar{w}_1 = 0$, $\bar{w}_2 = i|a_\kappa|$, and $\bar{w}_3 = -i|a_\kappa|$. For the coefficients A_i we obtain $A_1 = 0, A_2 = A_3 = \frac{1}{2}$. From (6.8) we then get

$$\bar{\tilde{\rho}}_\kappa(t) = \bar{\tilde{\rho}}_\kappa(t=0) \times \int_0^1 du\left(\frac{\partial}{\partial u}(u-1)\cos[\tfrac{1}{2}|a_\kappa|t(1-u)]\right) \times J_0(\sqrt{u}|a_\kappa|t)\,. \tag{6.10}$$

In order to evaluate the u integral, the cosine and Bessel functions are expanded into power series. With these calculations we arrive at

$$\bar{\tilde{\rho}}_\kappa(t) = \bar{\tilde{\rho}}_\kappa(t=0)J_0(|a_\kappa|t)\,. \tag{6.11}$$

In the site representation and for the initial condition $\rho_n(0) = \delta_{n0}$, we obtain from (2.11)

$$\rho_n(t) = \sum_k e^{i\kappa n}\frac{1}{N}J_0(|a_\kappa|t)\,. \tag{6.12}$$

For an infinite linear chain we finally arrive at the well-known[65] result

$$\rho_n(t) = J_n^2(2H_1 t)\,. \tag{6.13}$$

C. Solution in the purely incoherent case

We now have $|a_\kappa| = 0$ and the zeros of the denominator of (6.3) become $\bar{w}_1 = 0$, $\bar{w}_2 = -4\bar{\gamma}_1$, and $\bar{w}_3 = 4N\tilde{\gamma}_\kappa$. The coefficients A_i are simply $A_1 = A_2 = 0$, and $A_3 = 1$. From (6.8) we have

$$\bar{\tilde{\rho}}_\kappa(t) = \bar{\tilde{\rho}}_\kappa(t=0)\,e^{2N\tilde{\gamma}_\kappa t}\,, \tag{6.14}$$

and in the site representation and with nearest-neighbor interaction

$$\rho_n(t) = e^{-4\gamma_1 t}I_n(4\gamma_1 t)\,. \tag{6.15}$$

$I_n(4\gamma_1 t)$ is a modified Bessel function.[57]

D. Solution in the quasi-incoherent case $|a_\kappa| \ll \Gamma$

In this case the coherent interaction matrix elements are considered as a perturbation and the zeros of the denominator of (6.3) and the A_i's are calculated up to second order. In this way we obtain

$$\bar{w}_1 = -|a_\kappa|^2/4N\tilde{\gamma}_\kappa\,, \tag{6.16a}$$

$$\bar{w}_2 = -4\bar{\gamma}_1 + 2|a_\kappa|^2/(4\bar{\gamma}_1 + 4N\tilde{\gamma}_\kappa)\,, \tag{6.16b}$$

$$\bar{w}_3 = 4N\tilde{\gamma}_\kappa + |a_\kappa|^2(4\bar{\gamma}_1 - 4N\tilde{\gamma}_\kappa)/4N\tilde{\gamma}_\kappa(4N\tilde{\gamma}_\kappa + 4\bar{\gamma}_1)\,, \tag{6.16c}$$

and

$$A_1=|a_\kappa|^2/(4N\tilde{\gamma}_\kappa)^2\,, \tag{6.17a}$$

$$A_2=-2|a_\kappa|^2/(4\bar{\gamma}_1+4N\tilde{\gamma}_\kappa)^2\,, \tag{6.17b}$$

$$A_3=1+|a_\kappa|^2\frac{(4N\tilde{\gamma}_\kappa)^2-32N\bar{\gamma}_1\tilde{\gamma}_\kappa-(4\bar{\gamma}_1)^2}{(4N\tilde{\gamma}_\kappa)^2(4N\tilde{\gamma}_\kappa+4\bar{\gamma}_1)^2}\,. \tag{6.17c}$$

In this case it is more convenient to start the calculations from Eq. (6.6). Inserting (6.16) and (6.17) and taking into account only terms up to second order in $|a_\kappa|$, we have

$$\begin{aligned}\bar{\bar{\rho}}_\kappa(t)=\bar{\bar{\rho}}_\kappa(t=0)\frac{-2|a_\kappa|^2}{(4\bar{\gamma}_1+4N\tilde{\gamma}_\kappa)^2}\sum_{m=0}^{\infty}\frac{1}{m!}(-2\bar{\gamma}_1t)^m+\bar{\bar{\rho}}_\kappa(t=0)\frac{2|a_\kappa|^2}{(4\bar{\gamma}_1+4N\tilde{\gamma}_\kappa)^2}\sum_{m=0}^{\infty}\frac{1}{m!}(2N\tilde{\gamma}_\kappa t)^m\\ +\bar{\bar{\rho}}_\kappa(t=0)\sum_{m=0}^{\infty}\frac{1}{m!}(2N\tilde{\gamma}_\kappa t)^m\left(1-\frac{|a_\kappa|^2t}{4N\tilde{\gamma}_\kappa+4\bar{\gamma}_1}\right).\end{aligned} \tag{6.18}$$

The series in (6.18) may easily be summed, and up to second-order terms in $|a_\kappa|$ we may write

$$\bar{\bar{\rho}}_\kappa(t)=\bar{\bar{\rho}}_\kappa(t=0)\left\{\frac{-2|a_\kappa|^2}{(4\bar{\gamma}_1+4N\tilde{\gamma}_\kappa)^2}\exp(-2\bar{\gamma}_1t)+\frac{2|a_\kappa|^2}{(4\bar{\gamma}_1+4N\tilde{\gamma}_\kappa)^2}\exp(2N\tilde{\gamma}_\kappa\,t)+\exp\left[t\left(2N\tilde{\gamma}_\kappa-\frac{|a_\kappa|^2}{4N\tilde{\gamma}_\kappa+4\bar{\gamma}_1}\right)\right]\right\}. \tag{6.19}$$

For nearest-neighbor interaction and in the site representation we have with $\bar{\bar{\rho}}_\kappa(t=0)=N^{-1}$

$$\begin{aligned}\rho_n(t)=\int_{-\pi}^{\pi}\frac{d\kappa}{2\pi}\,e^{i\kappa n}\bigg\{\frac{-H_1^2(1-\cos\kappa)}{(\bar{\gamma}_1+N\tilde{\gamma}_\kappa)^2}\exp[-(2\Gamma+2\bar{\gamma}_1)t]+\frac{H_1^2(1-\cos\kappa)}{(\bar{\gamma}_1+N\tilde{\gamma}_\kappa)^2}\exp[-4\gamma_1t(1-\cos\kappa)]\\ +\exp\left[-\left(4\gamma_1+\frac{8H_1^2}{4\bar{\gamma}_1+4N\tilde{\gamma}_\kappa}\right)t(1-\cos\kappa)\right]\bigg\}.\end{aligned} \tag{6.20}$$

The first term in the curly brackets decays rapidly as compared to the remaining terms on account of $\Gamma=\gamma_0+2\gamma_1$ being much larger than γ_1. The relaxation times of the second and third terms are comparable; the prefactor of the second term, however, is under the conditions of this subsection much smaller than 1. The main contribution to $\rho_n(t)$ stems from the last term in (6.20). For the final evaluation of (6.20) we replace $\tilde{\gamma}_\kappa$ by $\tilde{\gamma}_0$, and on account of (1.8) and (1.13) we have $4N\tilde{\gamma}_\kappa\approx 4\Gamma$. The evaluation of (6.20) then gives:

$$\rho_n(t)\approx\exp\left[-\left(4\gamma_1+\frac{2H_1^2}{\Gamma+\bar{\gamma}_1}\right)t\right]I_n\left(\left(4\gamma_1+\frac{2H_1^2}{\Gamma+\bar{\gamma}_1}\right)t\right). \tag{6.21}$$

This approximate expression is the exact solution of the master equation (4.8), derived in the quasi-incoherent case. From the discussion of this section, however, we get an impression of the corrections in a more general case. (6.21) includes Kenkre's solution[41] as is immediately seen when setting $\gamma_1=\bar{\gamma}_1=0$.

VII. CONCLUDING REMARKS

In this paper we have presented an *exact* calculation of the kernel of the Nakajima-Zwanzig generalized master equation starting from the stochastic Liouville equation of the *full* Haken-Strobl model, describing the coupled coherent and incoherent motion of excitons in molecular crystals. In achieving at this result which is represented by Eq. (3.21), we have used a method, which allows an exact *straightforward* evaluation of the kernel of the generalized master equation. The basic equations are (1.15), (2.6), and (2.10). This is in contrast to recent calculations[41,43] of the kernels of generalized master equations, which start from simplified versions of the Haken-Strobl model and in which the solution of the corresponding stochastic Liouville equation has been used. In Figs. 1(a)–1(c) it is shown that the behavior of the generalized transition rates $K_1(\tau)$ and $K_m(\tau)$ for $m>1$ at the initial time is rather different: we have $K_1(\tau=0)\neq 0$ and $K_m(\tau=0)=0$ for $m>1$, which means that at the initial time we have generalized transition rates only between nearest neighbors and that with increasing time also transition rates between non-nearest neighbors arise. These additional transition rates (called long-range transfer rates in Refs. 41 and 43) occur in the GME because the non-diagonal elements of the density operator in the original stochastic Liouville equation have been eliminated. This rather different behavior of the transition rates for $m=1$ and $m>1$, however, is weakened when interactions also between non-nearest neighbors are taken into account; in this situation, those $K_m(\tau=0)$ are different from zero, for which the coherent interaction matrix elements $H_m \neq 0$.

Another interesting feature of the generalized transition rates is their damped oscillatory behavior with time. Physically these oscillations obviously arise from the superposition of coherent exciton waves. These properties are considerably changed when the Born approximation is used. Firstly, within this approximation only generalized transition rates exist having the same range as the coherent interaction matrix elements; especially in the case of nearest-neighbor interaction only K_1 is different from zero. Secondly, after applying the Born approximation, the kernels $K_m(t)$ simply decay exponentially with time and no longer show an oscillatory behavior. These results show that on account of the Born approximation a large part of the phase relations of the Liouville equation has been lost. The differences between the exact evaluation of the kernel and the result using the Born approximation are naturally most distinct, when the exciton motion is predominantly coherent. The importance of the Born approximation in evaluating the kernel of the GME is based on the fact that within this approximation the kernel, i.e., the memory function, may be determined from optical absorption and emission spectra.[35] The question now arises whether the kernel may also directly be derived from experimental data in cases where the Born approximation does not apply. This problem has also been discussed by Kenkre (see footnote 43 of Ref. 41).

Furthermore, the exact calculation of the mean-square displacement (5.7), taking into account the interaction with an arbitrary number of neighbors shows that in this expression the complicated behavior in time of the kernel of the GME is replaced by a term which increases linearly with time and a sum of decaying exponentials. We have discussed that experimental data available at present from diffusion measurements allow only the determination of the prefactor of the linear term (diffusion coefficient) and that, therefore, from these data alone one cannot decide whether the exciton motion is coherent or incoherent.

Finally, in this paper we have written the solution of the GME in a form which in some experimentally important cases may be evaluated analytically. In the general case the final evaluation amounts to determining the roots of a cubic equation and to the calculation of a double integral; both steps may easily be carried through numerically.

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