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Interpolation Formula for Propagators in Systems with Intermediate Degree of Transport Coherence*

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We present an interpolation formula for the probability propagators of the generalized master equation appropriate for the description of the motion of quasiparticles in systems with an intermediate degree of transport coherence. Although highly simplified in form, the formula is convenient for practical computations on complex systems whose exact dynamics would be essentially impossible to obtain. The formula has features analogous to some in the relaxation time prescription for the calculation of the Boltzmann distribution function. We point out the manner in which the interpolation formula may be used in conjuction with experimental data as well as with model calculations.

1. Introduction and the Interpolation Formula

Although the motion of quasiparticles such as Frenkel excitons in molecular crystals or excitations in biological systems has been actively investigated for many years with special attention on the issue of transport coherence [1–5], very few exact solutions valid for the entire intermediate range of coherence exist. Transport behaviour is understood in detail in the completely incoherent limit where a Master equation (sometimes referred to as the Pauli master equation) is the underlying equation of motion. Transport is also understood in the purely coherent limit where the Schrödinger equation among site states is operative. In addition, prescriptions [6, 7] are available which take these two starting points and, on the basis of a perturbation scheme, describe transport near those two limits, i.e., respectively, the largely incoherent limit and the largely coherent limit. And yet, many real systems exist, in which none of these available prescriptions and solutions is useful because the systems are too complex to be solved exactly and too far removed from both extreme limits to be approached through the approximation prescriptions. In this paper we suggest that in some of these cases an interpolation formula (to be used in the entire intermediate range) which is constructed starting from known solutions in the two limits might be useful. We examine several forms of such a formula, compare its consequences to some exact solutions, and discuss how it might be used in the light of experimental observations such as sensitized luminescence or transient grating.

For reasons that we will discuss below, we choose the probability propagators rather than intermediate quantities such as memory functions, as the objects on which to construct the interpolation formula. By the propagator, which we denote by $\psi_{mn}(t)$, is meant the probability that the quasiparticle occupies site m at time t, given that it occupied site n at time 0. We suppose that, for the system under consideration, the propagator is known for the case of complete coherence as also for the case of complete incoherence and we denote it in the two respective cases by $\psi^{c}_{mn}(t)$ and $\psi^{\mathrm{inc}}_{mn}(t)$. Our suggestion is that the intermediate range be described by the following expression for the propagator:

$$\psi_{mn}(t)=\psi^{\mathrm{inc}}_{mn}(t)+\xi(t)\left[\psi^{c}_{mn}(t)-\psi^{\mathrm{inc}}_{mn}(t)\right]. \qquad (1.1)$$

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Equation (1.1) contains the interpolation function $\xi(t)$ which we introduce. Its essential property is that it equals 1 at $t=0$ and tends to 0 as $t\to\infty$. By construction, therefore, the propagator ψ_{mn} as given by the interpolation formula (1.1) becomes identical to the known coherent propagator $\psi^{c}_{mn}(t)$ for $t\to 0$ and to the known incoherent propagator $\psi^{\rm inc}_{mn}(t)$ for $t\to\infty$, thus recovering the two limits in the appropriate extremes. While (1.1) would be at best a highly simplified version of the actual propagator in general, it is guaranteed to provide the correct description near the two limits and furthermore serves as a *single* prescription which spans the two limits. Whether or not the actual dynamics is described properly by (1.1) deep inside the intermediate range will be governed by how appropriate it is to assume a single function ξ to bridge all the propagators. In other words, it is always possible to write

$$\psi_{mn}(t)=\psi^{\rm inc}_{mn}(t)+\xi_{mn}(t)[\psi^{c}_{mn}(t)-\psi^{\rm inc}_{mn}(t)], \quad (1.2)$$

where we have introduced a separate interpolation function $\xi_{mn}(t)$ for every propagator. Since (1.2) would serve as a definition for $\xi_{mn}(t)$, the validity of (1.2) cannot be questioned. By the same token, however, (1.2) would be useless as it stands unless there were a simple *independent* way to arrive at the ξ's. We shall investigate below the consequences of (1.1), i.e. of assuming a single $\xi(t)$, particularly with simple choices for the time dependence of $\xi(t)$.

2. Consequences of the Exponential Form for $\xi(t)$

The requirements that the interpolation function ξ must satisfy in order that (1.1) be able to recover the appropriate limits at very short and very long times are

$$\xi(t\to 0)=1; \qquad \xi(t\to\infty)=0. \quad (2.1)$$

The simplest such function is the exponential:

$$\xi(t)=\exp(-\zeta t) \quad (2.2)$$

where ζ is a positive parameter to be determined from the dynamics of the system. The interpolation formula (1.1) now takes on a form which is highly analogous to the well-known relaxation time formula for the Boltzmann distribution function $f_k(t)$:

$$f_k(t)=f_k^{\infty}+(f_k^{0}-f_k^{\infty})\exp(-t/\tau). \quad (2.3)$$

The ζ we have introduced is analogous to the reciprocal of the relaxation time τ. The shortcomings of assuming a single ζ for all ψ's and a monotonically decreasing function such as an exponential for $\xi(t)$ are thus very similar to the shortcomings of assuming a single τ for all f's and an exponential form for the decay of the distribution functions in the Boltzmann equation context. The limits bridged by our interpolation prescription are the (time-dependent) coherent and incoherent propagators valid at short and long times respectively, whereas those bridged by the well-known relaxation time are the initial and final (thermalized) values of the distribution function. With this connection which might help in establishing the proper perspective on our interpolation formula (1.1), we now proceed to calculate its consequences.

Consider a dimer with equienergetic sites 1 and 2 wherein an exciton moves via the intersite matrix element V in the coherent limit and via the transfer rate F in the incoherent limit. The self-propagator $\psi_{11}=\psi_{22}\equiv\psi_0$ is given in the two extremes by [3]

$$\psi^{c}_{0}(t)=(1/2)[1+\cos(2Vt)], \quad (2.4)$$

$$\psi^{\rm inc}_{0}(t)=(1/2)[1+\exp(-2Ft)]. \quad (2.5)$$

We assume the destruction of the off-diagonal elements of the density matrix [2] at rate α. This assumption giving the $\exp(-\alpha t)$ damping of the coherent memory functions leads to the relation [3] $F=2V^2/\alpha$.

The interpolation formula (1.1) takes the form

$$\psi_0(t)=(1/2)\{[1+\exp(-2Ft)]+[\cos(2Vt)-\exp(-2Ft)]\exp(-\zeta t)\}. \quad (2.6)$$

The exact consequence of a stochastic Liouville equation description of motion in a dimer with α as the scattering rate is [3]

$$\psi_0(t)=[1+g(t)\exp(-\alpha t/2)]/2, \quad (2.7)$$

where $g(t)$ equals $(1+\alpha t/2)$ if $\alpha=4V$, and $[\cos(bt)+\alpha/(2b)\sin(bt)]$ with $b=(4V^2-\alpha^2/4)^{1/2}$ otherwise. On comparison of (2.6) and (2.7) with the prescription $F=2V^2/\alpha$, numerical calculations show that the best agreement is achieved for $\zeta=\alpha/2$ (see Fig. 1).

Consider now the infinite linear chain with the nearest neighbour interaction V whose exact self-propagator for arbitrary α calculated from the stochastic Liouville equation equals [7]

$$\psi_0(t)=e^{-\alpha t}J_0^2(2Vt)+\int_0^t \alpha e^{-\alpha(t-u)}J_0^2[2V(t^2-u^2)^{1/2}]\,du. \quad (2.8)$$

The approximate propagator given by Eqs. (1.1) and (2.2) is equal to

$$\psi_0(t)=[\exp(-2Ft)]I_0(2Ft)+[J_0^2(2Vt)-\exp(-2Ft)I_0(2Ft)]\exp(-\zeta t). \quad (2.9)$$

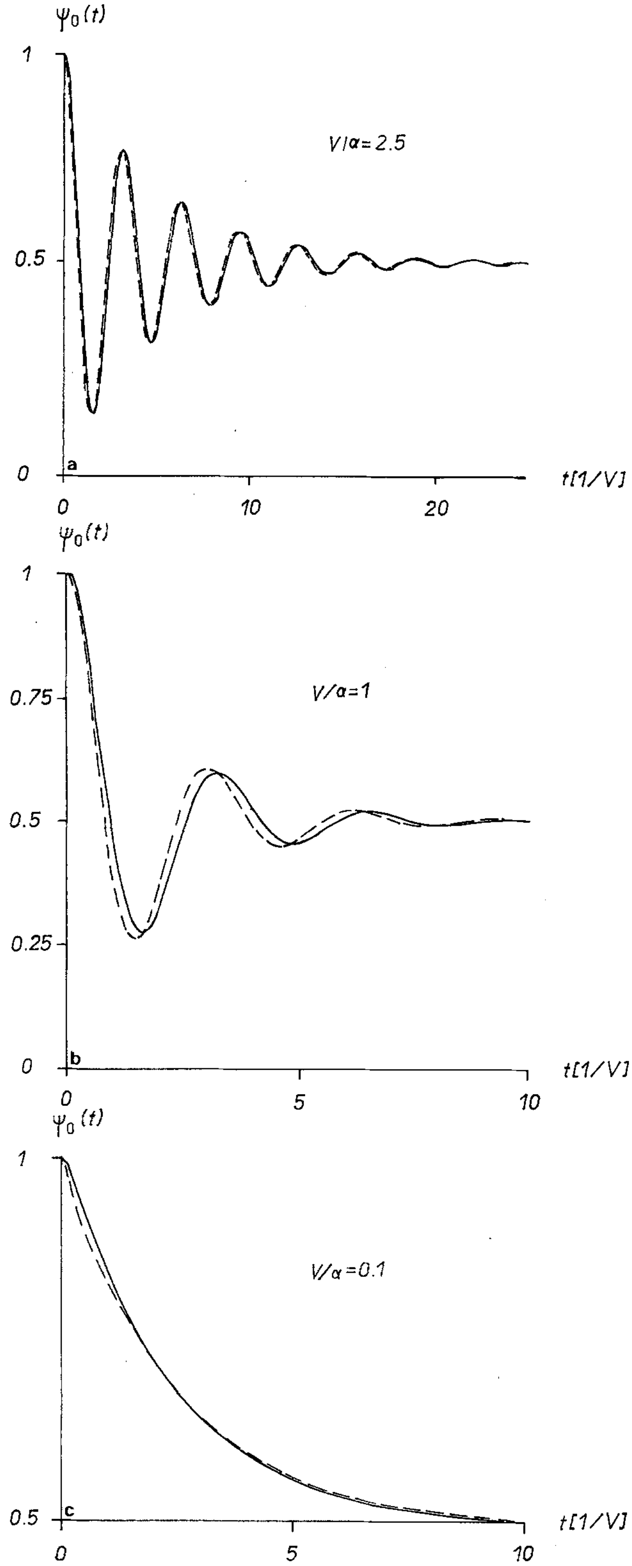


Fig. 1a–c. Comparison of the exact solution of the stochastic Liouville equation (full line) and the result of our interpolation prescription (dashed line) for the self-propagator $\psi_0(t)$ for the *dimer:* Three cases corresponding to large **(a)**, intermediate **(b)** and small **(c)** degree of the coherence (V/α) are shown. The value of the interpolation parameter ζ used in the figure is $\alpha/2$ and produces the most appropriate fit

As in case of the dimer we shall take $F=2V^2/\alpha$ for comparison. Numerical calculations lead to $\zeta=\alpha$ for best agreement (see Fig. 2).

We now use the interpolation formula for the calculation of the mean square displacement $\langle x^2\rangle$. The mean square displacement in the infinite linear chain with the propagator (2.8) equals [3] $2V^2a^2t^2$ in the coherent case, $2Fa^2t$ in the incoherent case, and, in the general case is given by

$$\langle x^2\rangle/a^2=[4V^2t/\alpha]-(4V^2/\alpha^2)(1-\exp(-\alpha t)), \qquad (2.10)$$

where a is the lattice constant. The interpolation formula for the mean square displacement reads

$$\langle x^2\rangle/a^2=2Ft+2(V^2t-F)te^{-\zeta t}. \qquad (2.11)$$

The comparison of $\langle x^2\rangle$ as given by (2.10) and (2.11) for the prescriptions $F=2V^2/\alpha$ and $\zeta=\alpha$ is shown in Fig. 3.

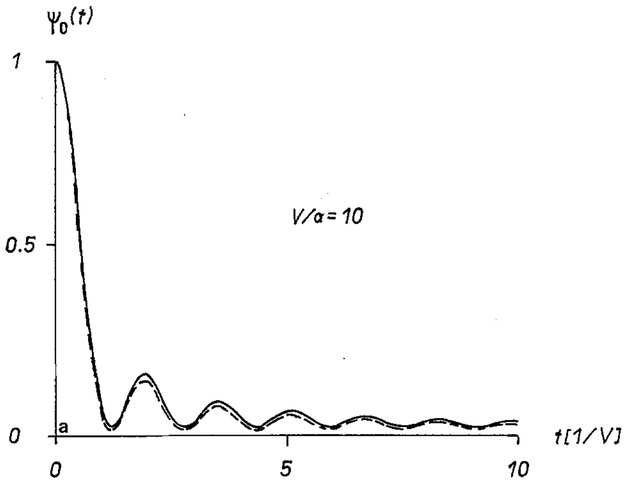
We see that while both curves have similar parabolic form for small t, they are shifted by a constant value for large t. This shift is unimportant and the diffusion constant D which equals (1/2) the infinite t limit of $d\langle x^2\rangle/dt$, is $2V^2a^2/\alpha$ in both cases.

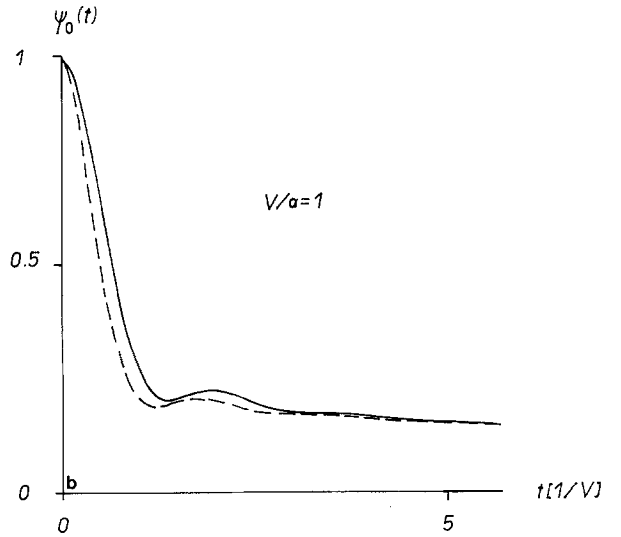
Finally, we analyze a situation in which the exact solutions in the intermediate range are much less poorly known than in the two limits of extreme coherence and incoherence thus presenting an explicit example of the interpolation scheme in a practical case. Consider a finite linear chain of N molecules in which the exciton would move via the nearest-neighbour interaction V in the coherent limit and via the nearest-neighbour transfer rate F in the incoherent limit. In contrast to the dimer and infinite linear chain the analytic solution for general α is not known in this case so that the interpolation formula seems to be the only way to describe at least approximately the corresponding propagators. The incoherent probability propagators are known [9] in the Laplace domain. The coherent propagators can also be calculated in the following way. The (coherent) *amplitude* propagator χ^c_{mn} equals

$$\tilde{\chi}^c_{mn}(\varepsilon)=\sum_{p=1}^{N} c^{(p)}_m c^{(p)}_n \frac{1}{\varepsilon+\mathrm{i}E_p t}, \qquad (2.12)$$

where $c^{(p)}_m=\sqrt{\frac{2}{N+1}}\sin\frac{mp\pi}{N+1}$ is the solution of the Schrödinger equation corresponding to the energy $E_p=2V\cos\frac{p\pi}{N+1}$, $p=1,\dots,N$ [10]. The propagator (2.12) can be summed [11] as

$$\tilde{\chi}^c_{mn}(\varepsilon)=\frac{i}{V}\frac{\sin(m\vartheta)\sin(N+1-m)\vartheta}{\sin\vartheta\sin(N+1)\vartheta}, \qquad m\leq n, \qquad (2.13)$$





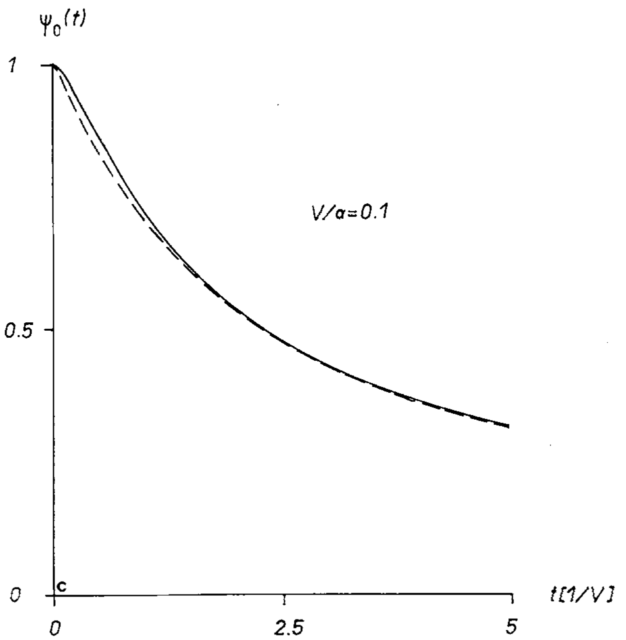


Fig. 2a–c. Comparison of the exact (full line) and the result of the interpolation prescription for the self-propagator $\psi_0(t)$ for the *infinite linear chain:* Three cases corresponding to large **(a)**, intermediate **(b)** and small **(c)** degree of the coherence (V/α) are shown. The value of ζ used in the figure is α (and not $\alpha/2$ as in Fig. 1) and provides the most appropriate fit. The results for the propagators $\psi_m(t)$ $(m \neq 0)$ are similar but not shown

where $\vartheta = \arccos(i\varepsilon/2V)$. A numerical Laplace inversion of (2.13) gives $\chi_{mn}(t)$ and thence the probability propagator $|\chi_{mn}(t)|^2$. A numerical inversion of the result in Ref. 9, on the other hand, gives the incoherent probability propagator. From the two limits the interpolation prescription yields the propagator for intermediate coherence through (1.1) and (2.2). The results are plotted in Fig. 4 for two values of the interpolation parameters as shown.

We see from Figs. 1–3 that the interpolation prescription gives reasonable fits to the exact solutions of the stochastic Liouville equation. The fits are, as expected, particularly good near the highly coherent and highly incoherent limits respectively. In the region far from both limits the approximation does not produce absurd or patently incorrect propagators. For complex systems in which direct solution

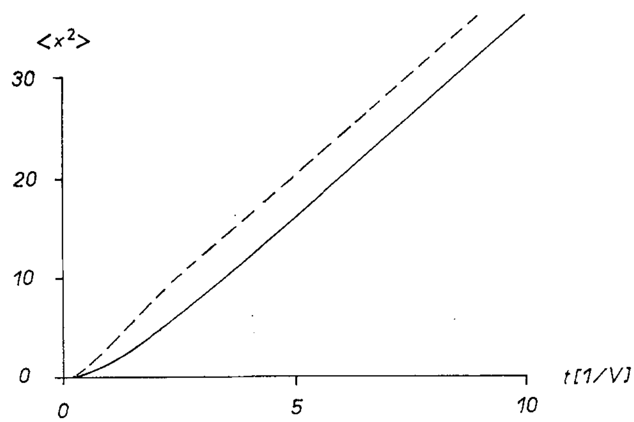


Fig. 3. The mean square displacement $\langle x^2 \rangle$ for the infinite linear chain as a function of time. The full line is the exact result while the dashed line results from the interpolation formula. The value of ζ used is α as in Fig. 2

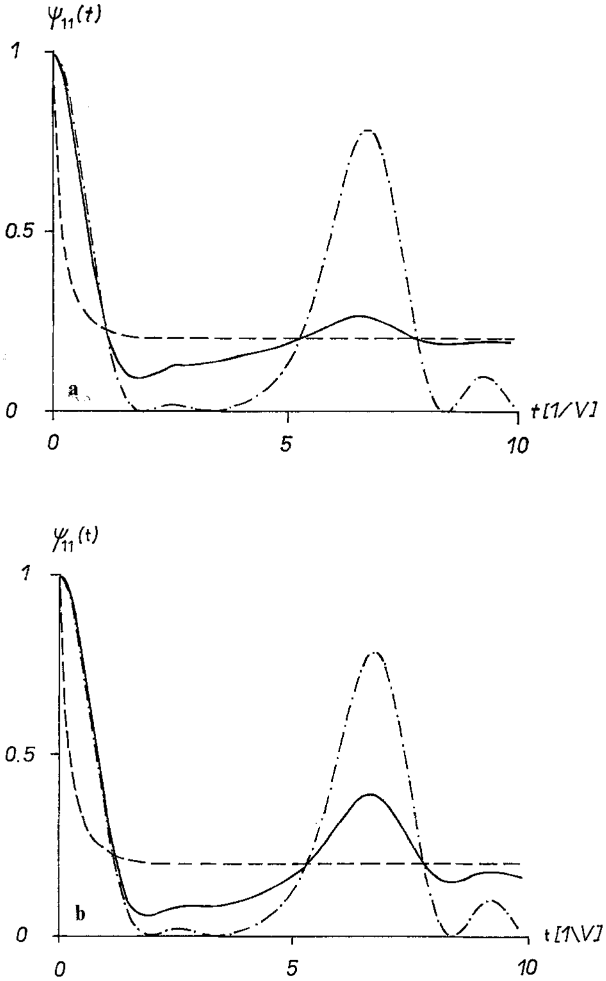


Fig. 4a and b. An example of the application of the interpolation prescription for a system for which the exact solution for arbitrary coherence is not known. Shown is the incoherent limit (dashed line), the coherent limit (dashed-dotted line) and the intermediate case using the interpolation formula. The values of the interpolation parameter are $\zeta=\alpha$ **(a)** and $\zeta=\alpha/2$ **(b)** respectively

for intermediate coherence is not practical we thus believe that the interpolation approximation might produce an acceptable description.

3. Extraction of ζ from Experimental Data

In systems for which the interpolation formula is appropriate, the value of the parameter ζ or the function $\xi(t)$ can be extracted easily from experimental observations. As examples we mention the transient grating signal and the (guest) quantum yield of luminescence. The former quantity is proportional to the square of $S(t)$, the amplitude of the sinusoidal inhomogenity in the exciton density produced by illuminating a crystal through crossed beams, whereas the latter is ϕ_G, the ratio of the number of photons that come out radiatively out of guest molecules which trap the excitons moving in a host crystal, to the number of photons put into the host initially through illumination.

The transient grating signal amplitude $S(t)$ is proportional to the Fourier transform of the propagators. Therefore, in terms of the interpolation formula and expressions S^c and S^{inc} which describe S in the coherent and incoherent limits respectively,

$$S(t)=S^{inc}(t)+[S^c(t)-S^{inc}(t)]\exp(-\zeta t). \tag{3.1}$$

Since both $S^c(t)$ and $S^{inc}(t)$ are well known from earlier analyses [12], one may write down ζ directly from experiment. Thus,

$$\begin{aligned}\exp(-\zeta t)&=\{S(t)-\exp[-4Ft\sin^2(\eta/2)]\}\\&\cdot\{J_0[4Vt\sin(\eta/2)]-\exp[-4Ft\sin^2(\eta/2)]\}^{-1}\end{aligned} \tag{3.2}$$

and ζ may be obtained by inspection or integration of the above expression from the observed transient grating input $S(t)$ on one hand and from known values of the intersite nearest-neighbour interaction V and the incoherent transfer rate F on the other. In (3.2) above, η is the ratio of the grating wavevector to the nearest-neighbour distance.

Unlike the transient grating signal $S(t)$ which is linear in the propagator transform, the quantum yield in sensitized luminescence is related to the propagator in a more complex fashion. Thus, in terms of the guest concentration ρ, the capture rate c, and the Laplace transform of the self-propagator evaluated at $\varepsilon=1/\tau$, where τ is the exciton lifetime, the guest yield is given by [2, 3]

$$\phi_G=\rho\tau[(1/c)+\tilde{\psi}_0(1/\tau)]^{-1}. \tag{3.3}$$

However, it is clear that the (observable) quantity $(\rho\tau/\phi_G)$ is linear in the Laplace transform of the propagator. Since the interpolation formula (1.1) for the self-propagator can be written in the Laplace domain as

$$\tilde{\psi}_0(\varepsilon)=\tilde{\psi}_0^{inc}(\varepsilon)+[\tilde{\psi}_0^c(\varepsilon+\zeta)-\tilde{\psi}_0^{inc}(\varepsilon+\zeta)] \tag{3.4}$$

the relation

$$\begin{aligned}(\rho\tau/\phi_G)=&(1/c)+\tilde{\psi}_0^{inc}(1/\tau)+[\tilde{\psi}_0^c(\zeta+1/\tau)\\&-\tilde{\psi}_0^{inc}(\zeta+1/\tau)]\end{aligned} \tag{3.5}$$

can be used at once to extract ζ from experiment. Expressions for $\tilde{\psi}_0^c(\varepsilon)$ and $\tilde{\psi}_0^{inc}(\varepsilon)$ are available [2] in terms of known special functions for simple models and may be used directly in (3.5) to extract ζ from known values of c, τ and ρ, and of the motion parameters F and V in the two limits.

4. Discussion

The interpolation prescription we have suggested and analyzed in this paper is not as microscopic in nature as the standart procedures (see e.g. Refs. 2, 3, 6, 7) in which the passage from the limits to the intermediate range of coherence occurs at the level of the memory functions or of the density matrix equations. Instead, our present prescription operates at the semi-microscopic level of the probability operators. While this is a relative shortcoming of the present method, it has also some practical advantages. Thus, when the interpolation function $\xi(t)$ is taken to have an appropriate form such as the exponential $\exp(-\zeta t)$, the interpolation propagators are guaranteed to satisfy the requirement that they lie between 0 and 1 at all times. It is interesting to compute the memory functions that correspond to the interpolation scheme. Since, for a periodic system, the Fourier transform of the propagator ψ^k is related to that of the memory functions $\mathscr{A}^k$ through [2, 3]

$$\tilde{\psi}^k(\varepsilon)=\frac{1}{\varepsilon+\tilde{\mathscr{A}}^k(\varepsilon)} \tag{4.1}$$

an expression analogous to (3.4) leads immediately to

$$\begin{aligned}\tilde{\mathscr{A}}^k(\varepsilon)=&\tilde{\mathscr{A}}_k^c(\varepsilon+\zeta)[\tilde{\mathscr{A}}_k^{\text{inc}}\,\zeta+(\varepsilon+\tilde{\mathscr{A}}_k^{\text{inc}})^2\\&+\tilde{\mathscr{A}}_k^{\text{inc}}\,\zeta(\zeta+2\varepsilon\tilde{\mathscr{A}}_k^{\text{inc}})]/[\tilde{\mathscr{A}}_k^c(\varepsilon+\zeta)\zeta\\&+\zeta^2+\zeta(2\varepsilon+\tilde{\mathscr{A}}_k^{\text{inc}})+(\varepsilon+\tilde{\mathscr{A}}_k^{\text{inc}})^2].\end{aligned} \tag{4.2}$$

To obtain (4.2) we have substituted the Fourier transform of the propagator given by the interpolation scheme of (1.1) and (2.2) in (4.1).

It is obvious from (4.2) that $\tilde{\mathscr{A}}^k(\varepsilon)$ is rather different from the coherent memory functions displaced at the Laplace domain. In other words the interpolation scheme produces a memory function which in general differs considerably from the one obtained at the microscopic level [2, 3] via exponential damping. Indeed, the former displays multiple time constants whereas the latter has a single time constant relevant to the onset of incoherence. To describe intermediate coherence the standard procedure [2, 3] uses a simple modification of the memory function and results in a complex modification of the propagators (see e.g. (2.8)), whereas the interpolation scheme presented here uses a simple modification of the propagators and results in a complex modification of the memory functions (as seen in (4.2)).

The propagators $\psi_{mn}(t)$ given by the prescription (1.1) fulfil the initial condition $\psi_{mn}(0)=\delta_{mn}$ and converge to the equilibrium values given by $\psi_{mn}^{\text{inc}}(t\to\infty)$. It follows from (4.2) that $\mathscr{A}^k(t\to\infty)=\lim_{\varepsilon\to 0}\varepsilon\tilde{\mathscr{A}}^k(\varepsilon)=0$ so that the corresponding memory functions go correctly to zero for $t\to\infty$. From this point of view, the interpolation formula (1.1) provides correct description for $t\to 0$ and ∞ limits.

There is no doubt that a modification at the memory function level is preferable in that one may relate it to features of the Hamiltonian such as exciton-phonon interactions in a straightforward way and that, whereas the parameter α which produces damping of the memory functions [2, 3] is essentially the rate of scattering of excitons, the interpolation parameter ζ has no such microscopic significance. The value of the interpolation formula lies, however, in its simplicity. It avoids the mathematically difficult problem of the solution of the equations of motion to get the propagator. For a given system, one may obtain ζ and $\xi(t)$ from one experiment, as shown in Sect. 3, and then use it for addressing another experiment. We believe that the interpolation procedure will be particularly useful for complex biological systems e.g. photosynthetic units where the solution of the equations of motion is not practical. The 5-molecule system we have studied in Fig. 4 is a simple example of such a situation.

Figures 1–3 and the relevant numerical calculations show that $\zeta=\alpha$ gives the best fit of the interpolation to the exact solution for large systems but $\zeta=\alpha/2$ gives the best fit for a dimer. It is conceivable that the propagator generally has several exponents in its behaviour which lie between these 2 values. In the 5-molecule chain we have therefore shown both $\zeta=\alpha/2$ and $\zeta=\alpha$ fits. It is to be noted that in the light of the results it may not be unreasonable to *calculate* ζ from scattering interactions in the same way that α or the relaxation time in the Boltzmann equation is calculated. Through such a calculation ζ may be obtained microscopically.

In conclusion, we have presented a simple scheme to describe motion with arbitrary degree of coherence to be used in complex systems. Undoubtedly there are situations in which the scheme will provide a poor description because it is not microscopic in character. However, it has a role which is similar to that of the relaxation-time approximation in the Boltzmann equation context and as such it is expected to be useful in systems where the more microscopic procedures are not practical.

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