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Theory of Transient Response for Arbitrarily Strong Driving Fields

BY MYRON W. EVANS*

Chemistry Department, University College of Wales, Aberystwyth, Dyfed SY23 1NE

AND

MAURO FERRARIO† AND PAOLO GRIGOLINI

Gruppo Nazionale di Struttura della Materia del C.N.R., Istituto di Fisica, Piazza Torricelli 2, 56100 Pisa, Italy

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A theory of the dynamical Kerr effect is developed for arbitrarily strong driving fields using a modification of the Mori equation of motion due to Grigolini *et al.* Using the multidimensional expansion of Grigolini and Ferrario the non-Markovian Mori equation may be written in Markov form. It is possible then to derive a macro–micro correlation theorem for the system by applying the method of Kivelson *et al.* In this way it is possible to bypass the linear response approximation of classical dielectric theory.

In this paper we describe a method for generalising the theory of radiationless and Kerr-effect transients [1] to include fields of arbitrarily large amplitude. The method used is one derived recently by Grigolini and Ferrario [2] to describe molecular systems where both "intramolecular" and "external" thermal baths are present (*e.g.*, resonant Raman scattering and resonant fluorescence). Measurements of emission spectra in the presence of strong driving fields may be used [3] in the same kind of way as saturation Kerr-effect studies to distinguish non-Markovian relaxations, especially of a radiationless nature, from the Markovian ones. Kerr-effect saturation is possible in polymer solutions with relatively low fields (E_0) where the total hamiltonian of the system would depend on powers of E_0 still not greater than the square.[4, 5] In this case the simplest theory put forward in this paper would suffice to describe the complicated transients observed recently [6] with Kerr-effect studies on polymer solutions. The shapes of these transients are concentration-dependent, implying that the simple Markovian theory (monodimensional) is not adequate to meet the new demands imposed by the latest available data.

THEORY

The hamiltonian of a spherical system in an external field can be written as

$$H = H_0 + H_1(t) = H_0 - \tfrac{1}{2}N\alpha^* E_0^2 - \tfrac{1}{3}(\alpha_\parallel^* - \alpha_\perp^*)E_0^2(t) \sum_{n=1}^{N} P_2(\cos\theta_i) \qquad (1)$$

† Present address: Chemistry Department, University College of Wales, Aberystwyth, Dyfed SY23 1NE.

which describes the Kerr effects to powers of E_0^2. The parameters α^* are effective polarisabilities independent of the field intensity E_0; N is the number of molecules. The third term on the right hand side of eqn (1) accounts for the interaction between the symmetry axis of the jth molecule and polarisation direction of the external field. Here θ_i denotes the angle between the ellipsoidal axis and the external field $E_0(t)$. The observable of interest is

$$A_M = K \sum_{i=1}^{N} P_2(\cos \theta_i) \tag{2}$$

where K is a constant defined in ref. (1). In evaluating the time evolution of the average value of this variable two significant simplifications are usually made. (1) The dynamical Kerr effect is linear in the perturbation provided by the fourth term and the r.h.s. of eqn (1). (2) The cross-correlation terms of the multi-particle correlation function

$$\Phi_M^{(i)} = \left\langle P_2[\cos \theta_i(0)] \sum_{j=1}^{N} P_2[\cos \theta_j(t)] \right\rangle \tag{3}$$

can be neglected.[7]

In this paper we provide a method capable of overcoming these assumptions using a theoretical technique developed for the treatment of an excitation–relaxation process in the presence of strong driving laser fields where the linear response approximation is no longer valid. Initially, we may assume that:

$$\langle A_M \rangle = N \sum_i \langle A_S^{(i)} \rangle \tag{4}$$

where

$$A_S^{(i)} = KP_2(\cos \theta_i). \tag{5}$$

The Mori formalism [8, 9] provides us with the time evolution of the $A_S^{(i)}$ variable in the presence of a strong external perturbation. Following Nordholm and Zwanzig [10] we define a Hilbert space whose vectors are the dynamical variables $A_i(t)$, $i = 1, \ldots, n$. This Hilbert space is not unique, in that it depends upon the definition of scalar product. Defining this conventionally, we may use the projection operator $\hat{P}$ on the subspace spanned by the variables $A_i(0)$

$$\hat{P}\boldsymbol{g} = (\boldsymbol{g}, \boldsymbol{A}^{\mathrm{T}})(\boldsymbol{A}, \boldsymbol{A}^{\mathrm{T}})^{-1}\boldsymbol{A}, \quad \boldsymbol{A} = \boldsymbol{A}(0)$$

where $\boldsymbol{g}$ is a vector in the Hilbert space. Apply this now to the Liouville equation:

$$\frac{\partial}{\partial t}\rho(t) = -\mathrm{i}\mathscr{L}(t)\rho(t) = -\mathrm{i}[H(t), \rho(t)] \tag{6}$$

where $\rho(t)$ is the density matrix and the Liouville operator $\mathscr{L}(t)$ is defined as the commutator superoperator associated with the hamiltonian $H(t)$. The latter may be divided into time-dependent and independent parts:

$$H(t) = H_0 + H_1(t).$$

H_0 describes the system as isolated, while $H_1(t)$ represents the interaction of the system with an external field. Operating with $\hat{P}$ on eqn (6) gives:

$$\frac{\partial}{\partial t}\hat{P}\rho(t) = -\hat{P}\mathrm{i}\mathscr{L}_0\hat{P}\rho(t) + \int_0^t [\hat{P}(-\mathrm{i}\mathscr{L}_0)\exp\{-(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0(t-s)\}\times (\hat{1}-\hat{P})(-\mathrm{i}\mathscr{L}_0)\hat{P}\rho(s)]\,\mathrm{d}s - \hat{P}\mathrm{i}\mathscr{L}_0 \exp\{-(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0 t\}(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0 A(0). \tag{7}$$

Using now the average value:

$$\langle A(t)\rangle = (A, \hat{P}\rho(t))$$

we obtain:

$$\frac{\mathrm{d}}{\mathrm{d}t} A(t) = (\hat{P}\mathrm{i}\mathscr{L}_0 A, A^{\mathrm{T}})(A, A^{\mathrm{T}})^{-1}A(t) + \int_0^t (\hat{P}\mathrm{i}\mathscr{L}_0 \exp[(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0(t-s)](\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0 A, A^{\mathrm{T}})(A, A^{\mathrm{T}})^{-1}A(s)\,\mathrm{d}s + \exp[(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0 t](\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0 A(0). \tag{8}$$

In eqn (8), the perturbation liouvillian associated with $H_1(t)$, *i.e.*, $\mathscr{L}_1(t)$, will appear both in the " memory kernel " and the fluctuating force. We shall now describe a general method for solving eqn (6) in the presence of an arbitrarily strong perturbation, *i.e.*, to develop a theory of the dynamical Kerr-effect in the presence of saturating fields in the classical limit. In the absence of external perturbation, the Laplace transform of the memory kernel can be expressed in a Mori continued fraction form. This is obtained by giving a special emphasis to a set of vectors f_j, $j = 1, \ldots, N_0[f_j = A(0)]$ which allow an easy way of expanding the " memory kernel " of eqn (8). The projection operator $\hat{P}_j$ onto the subspace spanned by the corresponding vector f_j, $j = 1, \ldots, N_0$, is defined as before. This set of states is a complete vector space in the sense that its describes the relevant slow dynamics of the system. This implies the identity relation:

$$\sum_{j=1}^{N_0} \hat{P}_j = \hat{1}, \qquad \hat{P}_1 = \hat{P}.$$

This relation may be used to show that eqn (8) may be replaced by:

$$\frac{\mathrm{d}}{\mathrm{d}t} V^{\mathrm{M}}(t) = \Lambda_0 V^{\mathrm{M}}(t) - \gamma^{\mathrm{M}} V^{\mathrm{M}}(t) + F^{\mathrm{M}}(t) \tag{9}$$

where

$$V^{\mathrm{M}}(t) = \begin{bmatrix} f_1^{\mathrm{M}}(t) \\ f_2^{\mathrm{M}}(t) \\ \cdot \\ \cdot \\ \cdot \\ f_{N_0}^{\mathrm{M}}(t) \end{bmatrix}; \qquad F^{\mathrm{M}}(t) = \begin{bmatrix} \mathbf{0} \\ \mathbf{0} \\ \cdot \\ \cdot \\ \cdot \\ F_{N_0}(t) \end{bmatrix}$$

are $n \times N_0$-dimensional column vectors. The friction matrix γ^{M} is a $n \times N_0$-dimensional square matrix whose elements are all zero except for the final one, which is the matrix γ. Λ_0 is a $n \times N_0$-dimensional square matrix whose explicit form is to be determined. $f_1^{\mathrm{M}}(t)$ is the n-dimensional column vector to be related to the part of interest of the projected or " reduced " physical system. Eqn (9) describes a $n \times N_0$-dimensional Markov process, with the fluctuation–dissipation properties:

$$\langle F^{\mathrm{M}}(t)\rangle = \mathbf{0}$$

$$\langle F^{\mathrm{M}}(t)F^{\mathrm{M}}(s)\rangle = [\gamma^{\mathrm{M}}\langle V^{\mathrm{M}}(0)[V^{\mathrm{M}}(0)]^{\mathrm{T}}\rangle + \langle V^{\mathrm{M}}(0)[V^{\mathrm{M}}(0)]^{\mathrm{T}}\rangle(\gamma^{\mathrm{M}})^{\mathrm{T}}]\delta(t-s).$$

The projection operators $\hat{P}_j^{\mathrm{M}}$, $j = 1, \ldots, N_0$ are now expressed in the form:

$$(\hat{P}_j^{\mathrm{M}})_{km} = \delta_{jk}\delta_{jm}I, \qquad j, k, m = 1, \ldots, N_0$$

where $\boldsymbol{I}$ is the n-dimensional unit matrix. We may use the operator $\hat{P}_1^{\mathrm{M}}$ to obtain from eqn (9) the non-Markovian, Langevin equation driving the relaxation dynamics of

$$\hat{P}_1^{\mathrm{M}} V^{\mathrm{M}}(t) = \hat{P}^{\mathrm{M}} V^{\mathrm{M}}(t) = \begin{bmatrix} f_1^{\mathrm{M}}(t) \\ \mathbf{0} \\ \cdot \\ \cdot \\ \cdot \\ \mathbf{0} \end{bmatrix}.$$

This is

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{P}^{\mathrm{M}} V^{\mathrm{M}}(t) = \hat{P}^{\mathrm{M}} \Lambda_0{}^{\mathrm{M}} V \hat{P}^{\mathrm{M}}(t) + \int_0^t \hat{P}^{\mathrm{M}} \Lambda_0 \exp\left[(\hat{1}-\hat{P}^{\mathrm{M}})(\Lambda_0 - \gamma^{\mathrm{M}})(t-s)\right](\hat{1}-\hat{P}^{\mathrm{M}})(\Lambda_0-\gamma^{\mathrm{M}}) + \hat{P}^{\mathrm{M}}\Lambda_0 \exp\left[(\hat{1}-\hat{P}^{\mathrm{M}})(\Lambda_0-\gamma^{\mathrm{M}})t\right](\hat{1}-\hat{P}^{\mathrm{M}})V^{\mathrm{M}}(0) + \int_0^t \hat{P}^{\mathrm{M}}\Lambda_0 \exp\left[(\hat{1}-\hat{P}^{\mathrm{M}})(\Lambda_0-\gamma^{\mathrm{M}})(t-s)\right](\hat{1}-\hat{P}^{\mathrm{M}})F^{\mathrm{M}}(s)\,\mathrm{d}s. \quad (10)$$

Note that $\hat{P}^{\mathrm{M}}\gamma^{\mathrm{M}} = \mathbf{0}$; $\hat{P}^{\mathrm{M}} F^{\mathrm{M}}(t) = \mathbf{0}$. We now show that eqn (8) and (10) [and therefore eqn (8) and (9)] are fully equivalent, provided that:

$$(\Lambda_0)_{jk} = (\mathrm{i}\mathscr{L}_0 f_j, f_k^{\mathrm{T}})(f_k, f_k^{\mathrm{T}})^{-1} \quad (11)$$

and the matrix γ^{M} is suitably related to the N_0th order approximant of the Mori continued fraction.

PROOF

The equivalence of eqn (8) and (10) may be demonstrated by expanding the memory kernel. The memory kernel of eqn (8) may be written as

$$\boldsymbol{K}(t,s) = (\mathrm{i}\mathscr{L}_0 \exp\left[(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0(t-s)\right](\hat{1}-\hat{P})\mathrm{i}\mathscr{L}_0 A, A^{\mathrm{T}})(A, A^{\mathrm{T}})^{-1} = \boldsymbol{K}(t-s).$$

Using the properties of scalar products, $\boldsymbol{K}(t,s)$ may be expanded as follows:

$$K(t,s) = ((\mathrm{i}\mathscr{L}_0 - \hat{\gamma})A, f_k^{\mathrm{T}})(f_k, f_k^{\mathrm{T}})^{-1} \times \left[(\exp\left\{(\hat{1}-\hat{P})(\mathrm{i}\mathscr{L}_0-\hat{\gamma})(t-s)\right\}(\hat{1}-\hat{P})(f_k, f_j^{\mathrm{T}})(f_j, f_j^{\mathrm{T}})^{-1}\right] \times ((\mathrm{i}\mathscr{L}_0-\hat{\gamma})f_j, A^{\mathrm{T}})(A, A^{\mathrm{T}})^{-1}. \quad (12)$$

In eqn (11), and in the following, summation on repeated indices is understood. Using eqn (11); we may evaluate the section between the braces as:

$$\begin{aligned}
&(\exp\left\{(\hat{1}-\hat{P})(\mathrm{i}\mathscr{L}_0-\hat{\gamma})(t-s)\right\}(\hat{1}-\hat{P})f_k, f_j^{\mathrm{T}})(f_j, f_j^{\mathrm{T}})^{-1} \\
&= \sum_{n=0}^{\infty} \frac{(t-s)^n}{n!}((\hat{1}-\hat{P})f_k, {}_{\cdot}{}^{\mathrm{T}}{}_{m_1})(f_{m_1}, f_{m_1}^{\mathrm{T}})^{-1}((\mathrm{i}\mathscr{L}_0-\hat{\gamma})f_{m_1}, f_{l_1}^{\mathrm{T}}](f_{l_1}, f_{l_1}^{\mathrm{T}})^{-1} \times \\
&\qquad ((\hat{1}-\hat{P})f_{l_1}, f_{m_2}^{\mathrm{T}}) \ldots ((\mathrm{i}\mathscr{L}_0-\hat{\gamma}).{}_{m_n}, f_{l_n}^{\mathrm{T}})(f_{l_n}, f_{l_n}^{\mathrm{T}})^{-1} \times \\
&\qquad ((\hat{1}-\hat{P})f_{l_n}, f_j^{\mathrm{T}})(f_j, f_j^{\mathrm{T}})^{-1} \\
&= \sum_{n=0}^{\infty} \frac{(t-s)^n}{n!}(\hat{1}-\hat{P}^{\mathrm{M}})_{k,m_1}(\Lambda_0-\gamma^{\mathrm{M}})_{m_1,l_1}(\hat{1}-\hat{P}^{\mathrm{M}})_{l_1,m_2}\ldots(\Lambda_0-\gamma^{\mathrm{M}})_{m_n,l_n}(\hat{1}-\hat{P}^{\mathrm{M}})_{l_n,j} \\
&= \exp\left\{(\hat{1}-\hat{P}^{\mathrm{M}})(\Lambda_0-\gamma^{\mathrm{M}})(t-s)\right\}_{kl}(\hat{1}-\hat{P}^{\mathrm{M}})_{lj}.
\end{aligned}$$

Using this result in the memory kernel gives us eqn (12) immediately. Note that due to the orthogonality relation between the vectors f_j, Λ_0 is a tridiagonal supermatrix defined by:

$$\left.\begin{aligned}(\Lambda_0)_{j,j} &= \mathrm{i}\Omega_j = (\mathrm{i}\mathscr{L}_0 f_j, f_j^{\mathrm{T}})(f, f_j^{\mathrm{T}})^{-1}\\ (\Lambda_0)_{j,j+1} &= \mathbf{1} = (\mathrm{i}\mathscr{L}_0 f_j, f_{j+1}^{\mathrm{T}})(f_{j+1}, {}_{j+1}^{\mathrm{T}})^{-1}\\ (\Lambda_0)_{j+1,j} &= -\Delta_{j-1}^2 = (\mathrm{i}\mathscr{L}_0 f_{j+1}, f_j^{\mathrm{T}})(f_j, f_j^{\mathrm{T}})^{-1}\end{aligned}\right\}. \tag{13}$$

The operator $\hat{\gamma}$ is defined as follows:

$$(\hat{\gamma} f_j, f_k) = (\gamma^{\mathrm{M}})_{jl}(f_l, f_k^{\mathrm{T}}).$$

These results are equivalent to those of Kivelson and Ogan.[9]

To extend the formalism to the case where external fields are perturbing the system we have to tackle the following difficulties. (1) The physical system is no longer invariant to time reversal. This implies that (2) the memory kernel $\boldsymbol{K}(t, s)$ is no longer dependent on the difference $(t-s)$ but is a function of the two independent variables t and s. As the hamiltonian $H(t)$ is time dependent and in general $[H(t), H(t')] \neq 0$ for $t \neq 0$, the operator $\mathscr{L}_1(t)$ is no longer hermitian in the Hilbert space defined by the scalar products. Nordholm and Zwanzig [10] have shown that in this case (denoting by $\langle \ldots \rangle_t$ the average value at time t and by $\overrightarrow{\exp}$ a time-ordered exponential):

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle \boldsymbol{A}\rangle_t &= \langle \hat{P}\mathrm{i}\mathscr{L}(t)\boldsymbol{A}\rangle_t +\\ &\int_0^t \mathrm{d}s \left\langle \hat{P}\mathrm{i}\mathscr{L}(s)\,\overrightarrow{\exp}\left\{\int_s^t \mathrm{d}s_1(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}(s_1)\right\}(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}(t)\boldsymbol{A}\right\rangle_s +\\ &\left\langle \overrightarrow{\exp}\left\{\int_0^t \mathrm{d}s\,(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}(s)\right\}(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}(t)\boldsymbol{A}\right\rangle_0\\ &= (\hat{P}\mathrm{i}\mathscr{L}(t)\boldsymbol{A}, \boldsymbol{A}^{\mathrm{T}})(\boldsymbol{A}, \boldsymbol{A}^{\mathrm{T}})^{-1}\langle \boldsymbol{A}(t)\rangle +\\ &\int_0^t (\hat{P}\mathrm{i}\mathscr{L}(s)\,\overrightarrow{\exp}\left\{\int_s^t \mathrm{d}s_1\,(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}(s_1)\right\}(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}(t)(\boldsymbol{A}, \boldsymbol{A}^{\mathrm{T}})(\boldsymbol{A}, \boldsymbol{A}^{\mathrm{T}})\langle \boldsymbol{A}(s)\rangle +\\ &\left\langle \overrightarrow{\exp}\left\{\int_0^t (\hat{1}-\hat{P})\mathrm{i}\mathscr{L}(s)\,\mathrm{d}s\right\}(\hat{1}-\hat{P})\mathrm{i}\mathscr{L}(t)\boldsymbol{A}(0)\right\rangle.\end{aligned} \tag{14}$$

Eqn (9) may be rewritten [11] using the equivalent of eqn (11) in the presence of an external field:

$$(\Lambda_1(t))_{jk} = [\mathrm{i}\mathscr{L}_1(t)f_j, f_k^{\mathrm{T}}](_{,k}, f_k^{\mathrm{T}})^{-1} \tag{15}$$

In the N_0th-order approximation ($\sum_{j=1}^{N_0} = 1$), eqn (9) may be replaced by:

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{V}^{\mathrm{M}}(t) = [\Lambda_0+\Lambda_1(t)]\boldsymbol{V}^{\mathrm{M}}(t) - \gamma^{\mathrm{M}}\boldsymbol{V}^{\mathrm{M}}(t) + \boldsymbol{F}^{\mathrm{M}}(t). \tag{16}$$

We now prove the equivalence of eqn (14) and (16).

Proof: Project eqn (16) for the variable of interest, $P^{M}V^{M}(t)$

$$\frac{d}{dt}\hat{P}^{M}V^{M}(t) = \hat{P}^{M}[\Lambda_0+\Lambda_1(t)]\hat{P}^{M}V^{M}(t)+$$
$$\int_0^t \hat{P}^{M}[\Lambda_0+\Lambda_1(t)-\gamma^{M}]\overleftarrow{\exp}\left\{\int_s^t(\hat{1}-\hat{P}^{M})\times[\Lambda_0+\Lambda_1(s_1)-\gamma^{M}]\,ds_1\right\}\times$$
$$(\hat{1}-\hat{P}^{M})(\Lambda_0+\Lambda_1(s)-\gamma^{M})\hat{P}^{M}V^{M}(s)\,ds+$$
$$\overleftarrow{\exp}\left\{\int_0^t(\hat{1}-\hat{P}^{M})[\Lambda_0+\Lambda_1(s_1)-\gamma^{M}]\,ds_1\right\}(\hat{1}-\hat{P}^{M})V^{M}(0)+$$
$$\int_0^t \hat{P}^{M}[\Lambda_0+\Lambda_1(t)-\gamma^{M}]\overleftarrow{\exp}\left\{\int_s^t(\hat{1}-\hat{P}^{M})[\Lambda_0+\Lambda_1(s_1)-\gamma^{M}]\,ds_1\right\}\times$$
$$(\hat{1}-\hat{P}^{M})F^{M}(s)\,ds. \tag{17}$$

Then, expanding the memory kernel of eqn (14) on the set of the Mori variable $f_j, j-1, \ldots, N_0$:

$$K(t,s) = \left(\hat{P}i\mathscr{L}(s)\overrightarrow{\exp}\left\{\int_s^t(\hat{1}-\hat{P})i\mathscr{L}(s_1)\,ds_1\right\}(\hat{1}-\hat{P})i\mathscr{L}(t)A, A^{T}\right)(A, A^{T})^{-1}$$
$$= ((i\mathscr{L}(t)-\hat{\gamma})A, f_k^{T})(f_k, f_k^{T})^{-1}\times$$
$$\left[\left(\overrightarrow{\exp}\left\{\int_s^t(\hat{1}-\hat{P})(i\mathscr{L}(s_1)-\hat{\gamma})\,ds_1\right\}(\hat{1}-\hat{P})f_k, f_j^{T}\right)(f_j, f_j^{T})^{-1}\right]\times$$
$$((i\mathscr{L}(s)-\hat{\gamma})f_j, A^{T})(A, A^{T})^{-1}.$$

By focusing our attention on the contribution in square brackets, we obtain:

$$\left(\overrightarrow{\exp}\left\{\int_s^t(\hat{1}-\hat{P})(i\mathscr{L}(s_1)-\hat{\gamma})\,ds_1\right\}(\hat{1}-\hat{P})f_k, f_j^{T}\right)(f_j, f_j^{T})^{-1}$$
$$= \sum_{n=0}^{\infty}\frac{1}{n!}\int_s^t dt_1\ldots\int_s^t dt_n\,\{((\hat{1}-\hat{P})f_k, f_{m_1}^{T}](f_{m_1}, f_{m_1}^{T})^{-1}\times$$
$$((\hat{1}-\hat{P})(i\mathscr{L}(t_n)-\hat{\gamma})(\hat{1}-\hat{P})(i\mathscr{L}(t_{n-1})-\hat{\gamma})\ldots\times$$
$$\ldots(i\mathscr{L}(t_1)-\hat{\gamma})f_{m_1}, f_j^{T})(f_j, f_j^{T})^{-1}\}$$
$$= \sum_{n=0}^{\infty}\frac{1}{n!}\int_s^t dt_1\ldots\int_s^t dt_n\,\{((\hat{1}-\hat{P})f_k, f_{m_1}^{T})\times$$
$$(f_{m_1}, f_{m_1}^{T})^{-1}((i\mathscr{L}(t_1)-\hat{\gamma})f_{m_1}, f_{l_1}^{T})(f_{l_1}, f_{l_1}^{T})^{-1}\times$$
$$((\hat{1}-\hat{P})f_{l_1}, f_{m_2}^{T})(f_{m_2}, f_{m_2}^{T})^{-1}\ldots\times$$
$$((i\mathscr{L}(t_n)-\hat{\gamma})f_{m_n}, f_{l_n}^{T})(f_{l_n}, f_{l_n}^{T})^{-1}((\hat{1}-\hat{P})f_{l_n}, f_j^{T})(f_j, f_j^{T})^{-1}\}$$
$$= \sum_{n=0}^{\infty}\frac{1}{n!}\int_s^t dt_1\ldots\int_s^t dt_n\,\{(\hat{1}-\hat{P}^{M})_{k,m_1}\times$$
$$(\Lambda_0+\Lambda_1(t_1)-\gamma^{M})_{m_1,l_1}(\hat{1}-\hat{P}^{M})_{l_1,m_2}\times$$
$$\ldots(\Lambda_0+\Lambda_1(t_n)-\gamma^{M})_{m_n,l_n}(\hat{1}-\hat{P}^{M})_{l_n,j}\}$$
$$= \overleftarrow{\exp}\left\{\int_s^t ds_1\,[(\hat{1}-\hat{P}^{M})(\Lambda_0+\Lambda_1(s_1)-\gamma^{M})]\right\}_{k,l}(\hat{1}-\hat{P}^{M})_{l,j}$$

using eqn (15) and (11) for the third step. We therefore obtain:

$$K(t,s) = (\Lambda_0+\Lambda_1(t)-\gamma^{M})_{1k} \overleftarrow{\exp}\left\{\int_s^t ds_1\,(\hat{1}-\hat{P}^{M})(\Lambda_0+\Lambda_1(s_1)-\gamma^{M})\right\}_{kl} \times (\hat{1}-\hat{P}^{M})_{lj}(\Lambda_0+\Lambda_1(s)-\gamma^{M})_{j1}$$

which is exactly the memory kernel of eqn (17). This concludes the proof.

We can focus our attention on the projection operator which projects a generic vector V on the subspace spanned by the first variable of the chain of Markov variables. Using this operator, we can apply to eqn (16) the Mori methodology. It is possible to show [12] that the generalised master equation obtained is endowed with precisely the same memory kernel and the same fluctuating force as those appearing in eqn (14). It follows that eqn (16) may be used to describe the effect on the system of an arbitrarily strong driving field such as E_0 of eqn (1). Eqn (16) in turn may be solved by using the matrix diagonalisation approach of ref. (2). This treats the excitation–relaxation process without the usual approximations that the excitation field is weak and the time duration of the external perturbation is very short with respect to the relaxation times. It is interesting to remark [13, 14] that in the field of radiationless transitions in molecular condensed phases a time-dependent behaviour of the emitted fluorescence has been detected which is very similar to recent results on Kerr-effect transients in solutions of polyethylene glycol polymer. This type of transient behaviour may be explained in terms of the multi-dimensional Markov representation as follows. A three-state model may be constructed for the process where the intermediate is interpreted as a "virtual" state simulating the non-Markovian behaviour of the radiationless relaxation resulting from the coupling of the excited state of interest with an intramolecular dissipation continuum. The phenomenological approach of ref. (13) shows that high-intensity fields are required in order to explain the slow decay exhibited in the presence of the radiation field.

A macro–micro theorem connecting the decays of the multi-particle and single-particle correlation functions may now be constructed within the context of the multi-dimensional Markov representation by choosing vectors of the form $\begin{bmatrix} A_m \\ A_s \end{bmatrix}$ and proceeding (in the manner described by Kivelson *et al.*[4] and by Berne and Pecora)[15] to evaluate the relation theorem for the last variable of the Markov chain. The applications to Kerr effect and fluorescence transient data of the theory outlined here will be the subject of further work. We shall not develop the theorem here since this is secondary to our theme of treating arbitrarily strong driving fields.

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APPENDIX

In this appendix we discuss in greater detail the nature of the hamiltonian H appearing in eqn (1). The part H_0 of the hamiltonian involves intermolecular interactions. If we replace the collective variable A_m with the single one $A_s^{(i)}$ the relaxation process depends on the interaction among the ith molecule and the other molecules of the sample. In making the assumption:

$$\langle A_m\rangle = N\langle A_s^{(i)}\rangle$$

it is implied that any one molecule provides the same average value. We are disregarding the cross-correlation terms of $\Phi_m^{(1)}$ and assuming that the molecules i and $j(j\neq i)$ are not intereacting. The decay of the correlation function in such a case is

assured by the chaotic distribution of the molecules. That is, when one is performing the average on all the molecules of the sample then $\langle P_2 \cos\theta(0) P_2 \cos\theta(t)\rangle$ is exhibiting decay features resulting from the average itself. Even if it is assumed that the ith molecule is not interacting with the other molecules the autocorrelation function $\langle P_2 \cos\theta_i(t) P_2 \cos\theta_i(0)\rangle$ may decay only by averaging over effectively infinite number of other molecules in the system.

However, if any ith molecule of any sample is interacting with the other molecules the cross-contribution of $\Phi_m^{(1)}$ does not vanish. The autocorrelation function then decays both due to the average over the sample and due to the interaction with the other molecules. In the Mori theory the correlation function $\langle A \cdot A(t)\rangle$ is a scalar product which involves a statistical density matrix (or a distribution function). Its time evolution depends both on the initial conditions of the statistical density matrix (and the unperturbed hamiltonian) and the perturbation hamiltonian. As a consequence, the hamiltonian whose liouvillian appears in eqn (14) is that part of H_0 which concerns the ith particle plus

$$-\tfrac{1}{2}\alpha^* E_0^* - \tfrac{1}{3}(\alpha_\parallel^* - \alpha_\perp^*) E^2(t) P_i^N(\cos\theta_N).$$

Therefore, it is important to note that H in the present paper is that part of the hamiltonian of eqn (1) which involves the ith particle. We have to omit the contribution involving only $j \neq i$.

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