Master equations through cumulant techniques

1990 J. Phys. A: Math. Gen. 23 107

(http://iopscience.iop.org/0305-4470/23/2/008)

J. Phys. A: Math. Gen. **23** (1990) 107-115. Printed in the UK

Master equations through cumulant techniques

Adam J Makowski

Institute of Physics, Nicholas Copernicus University, ul. Grudziadzka 5/7, 87-100 Torun, Poland

Received 30 May 1989

Abstract. We discuss master equations of three types: with no memory at all, with a restricted memory and with a complete memory involved. They are derived with the help of cumulant expansions based on proper time orderings and are then applied to a simple collisional model. A general formula for matrix elements of the so-called TTO cumulants and low-order cumulants of other types is also proposed.

1. Introduction

One of the ways of deriving master equations starts from the Liouville equation $\partial\rho/\partial t = (-\mathrm{i}/\hbar)\Lambda\rho$, where $\Lambda\rho = [H, \rho]$ and H is the system Hamiltonian. This equation is then reduced so as to eliminate some quantities which can, in a way, be treated as irrelevant. To this end, suitable projection operators are usually applied [1] and as a result an equation of motion for the reduced density operator is derived.

Such a method can also be joined with the cumulant technique first introduced into physics by Kubo [2]. This idea has found many applications, e.g. in molecular [3] and spin [4, 5] relaxations, the theory of lineshapes [6] and the stochastic collision theory [7, 8].

It appeared that master equations derived in this fashion can be of two types. A local equation with no memory follows if the partial time ordering (PTO) [4, 8] prescription is chosen. Another equation is completely non-local in time (full memory) which is the result of the total time ordering (TTO) [5] prescription involved.

The possible ways of the time orderings are systematised in a recent paper [9] where it was shown that apart from the above-mentioned master equations there is a large class of equations with a restricted memory. They are based on a PTO-like expansion which we shall call the modified partial time ordering (MPTO).

Contrary to most treatments, we do not deal here with equations of motion for the reduced density operator itself but rather with those for its diagonal elements. The method of the reduction scheme used in this paper has been described in detail in [7]. We shall only mention essential points of the approach.

To this end, let us consider a dynamical system with degrees of freedom which can be divided into two classes of 'relevant' and 'irrelevant' ones, i.e. $H = H_\mathrm{i} + H_\mathrm{r} + H_\mathrm{ri}$. Concerning the r and i variables we assume that (i) interactions between all degrees of freedom in both groups vanish asymptotically ($t \to \pm\infty$) (ii) initially ($t_0 = -\infty$) the r and i quantities are not correlated. Moreover, the division of variables into two groups is done in such a way that the two subsystems are weakly correlated. This is usually the case when timescales related to the subsystems are quite different.

0305-4470/90/020107+09$03.50

Under the above assumptions it is not difficult to show [7] that the relevant part of the density operator in the interaction representation is given by

$$\sigma(t) = \mathrm{T}\exp\left(\frac{-\mathrm{i}}{\hbar}\int_{t_0}^{t} H'_{\mathrm{ri}}(t_1)\,\mathrm{d}t_1\right)\sigma(t_0)\exp\left(\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t} H'_{\mathrm{ri}}(t_1)\,\mathrm{d}t_1\right) \tag{1}$$

where

$$\sigma(t) = \exp[(\mathrm{i}/\hbar)\Lambda_{\mathrm{r}}(t-t_0)]\rho_{\mathrm{r}}(t)$$
$$\rho(t) = \rho_{\mathrm{i}}(t)\rho_{\mathrm{r}}(t) = \exp[-(\mathrm{i}/\hbar)\Lambda_{\mathrm{i}}(t-t_0)]\rho_{\mathrm{i}}(t_0)\rho_{\mathrm{r}}(t)$$
$$H'_{\mathrm{ri}}(t) = \exp[(\mathrm{i}/\hbar)\Lambda_{\mathrm{r}}(t-t_0)]H_{\mathrm{ri}}(t).$$

The symbol T stands for the Dyson chronological operator and H_{ri} describes an interaction between the two subsystems under consideration.

Now we project out the diagonal components of σ in a basis $|n\rangle$ defined by $H_{\mathrm{r}}|n\rangle = E_n|n\rangle$ and perform an ensemble average $\{\sigma(t)\} = \mathrm{Tr}_{\mathrm{i}}[\rho_{\mathrm{i}}(t_0)\sigma(t)]$ with $\mathrm{Tr}_{\mathrm{i}}\rho_{\mathrm{i}}(t_0) = 1$. Then assuming that the initial density matrix is diagonal in the n representation and denoting $\{\langle n|\sigma(t)|n\rangle\} = P_n(t)$, we get

$$P_n(t) = \sum_p \{M_{np}(t)\}P_p(t_0) \tag{2}$$

where

$$M_{np}(t) = \left|\left\langle n|\mathrm{T}\exp\left(\frac{-\mathrm{i}}{\hbar}\int_{t_0}^{t} H'_{\mathrm{ri}}(t_1)\,\mathrm{d}t_1\right)|p\right\rangle\right|^2. \tag{3}$$

In section 2 the two equations and the idea of cumulants will be used to derive master equations of three types. Section 3 deals with a general matrix representation of TTO cumulants. In section 4 we apply the master equations to a simple collisional model.

2. The survey of master equations

A very attractive method of deriving master equations is based on using the concept of cumulants. It consists, in our case, in re-expressing the matrix $\{\mathbf{M}(t)\}$ in terms of sums of cumulants:

$$\{\mathbf{M}(t)\} = \exp_0\left(\sum_k \left(\frac{-\mathrm{i}}{\hbar}\right)^k \int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{k-1}}\mathrm{d}t_k\boldsymbol{\Phi}^{(k)}(t_1, t_2, \ldots, t_k)\right). \tag{4}$$

The symbol $\boldsymbol{\Phi}^{(k)}$ stands for the kth-order cumulant operator of any type (see below) and the sum over k runs in general from one to infinity. All the lower limits of the integrals are the same and are equal to an initial time, say t_0. The subscript 0 of exp distinguishes between the appropriate ordering prescriptions. This becomes clear when $\{\mathbf{M}(t)\}$ is expanded in the form:

$$\{\mathbf{M}(t)\} = \mathbf{I} + \sum_k \left(\frac{-\mathrm{i}}{\hbar}\right)^k \int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{k-1}}\mathrm{d}t_k\boldsymbol{\Phi}^{(k)}(t_1, t_2, \ldots, t_k)$$
$$+\sum_k\sum_l \left(\frac{-\mathrm{i}}{\hbar}\right)^{k+l}\int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{k-1}}\mathrm{d}t_k\boldsymbol{\Phi}^{(k)}(t_1, t_2, \ldots, t_k)$$
$$\times\int^{t_\mu}\mathrm{d}t_{k+1}\int^{t_{k+1}}\mathrm{d}t_{k+2}\ldots\int^{t_{k+l-1}}\mathrm{d}t_{k+l}\boldsymbol{\Phi}^{(l)}(t_{k+1}, t_{k+2}, \ldots, t_{k+l})$$

$$+\sum_k\sum_l\sum_s\left(\frac{-\mathrm{i}}{\hbar}\right)^{k+l+s}\int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{k-1}}\mathrm{d}t_k\Phi^{(k)}(t_1,t_2,\ldots,t_k)$$
$$\times\int^{t_\mu}\mathrm{d}t_{k+1}\int^{t_{k+1}}\mathrm{d}t_{k+2}\ldots\int^{t_{k+l-1}}\mathrm{d}t_{k+l}\Phi^{(l)}(t_{k+1},t_{k+2},\ldots,t_{k+l})$$
$$\times\int^{t_{\mu+\nu}}\mathrm{d}t_{k+l+1}\int^{t_{k+l+1}}\mathrm{d}t_{k+l+2}\ldots\int^{t_{k+l+s-1}}\mathrm{d}t_{k+l+s}\Phi^{(s)}(t_{k+l+1},\ldots,t_{k+l+s})$$
$$+\ldots. \tag{5}$$

The next term in (5) and the general rule of the expansion are symbolically presented in table 1. The consecutive integers 0, 1, 2 and so on, stand for the upper limits t_0, t_1, t_2, ..., of the integrals in the expansion (5). Different time orderings are attributed to different values for the Greek indices μ, ν, δ etc.

Table 1. The symbolic representation of the first four terms in expansion (5).

First limit	Second limit	Third limit		$(k-1)$th limit	kth limit
0	1	2	...	$k-2$	$k-1$
μ	$k+1$	$k+2$	...	$k+l-2$	$k+l-1$
$\mu+\nu$	$k+l+1$	$k+l+2$	...	$k+l+s-2$	$k+l+s-1$
$\mu+\nu+\delta$	$k+l+s+1$	$k+l+s+2$	...	$k+l+s+p-2$	$k+l+s+p-1$

For the choice $\mu=k$, $\nu=l$, $\delta=s$ etc, we get the well known TTO expansion [5]. Here, the order of time limits is total. As we have shown previously [9], this leads to the generalised non-local master equation with complete memory

$$\frac{\mathrm{d}P_n}{\mathrm{d}t}=\sum_{s=1}^{\infty}\sum_p\left(\frac{-\mathrm{i}}{\hbar}\right)^{s+1}\int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{s-1}}\mathrm{d}t_s\theta_{np}^{(s+1)}(t,t_1,\ldots,t_s)P_p(t_s) \tag{6}$$

where the matrix elements of the TTO cumulants are denoted by $\theta_{np}^{(s+1)}$.

Another choice is given by the values $\mu=1$, $\mu+\nu=k+1$, $\mu+\nu+\delta=k+l+1$ etc, i.e. the Greek indices from the first column in table 1 are replaced by the proper values from the second one. Now, the chronological order of the upper time limits is only preserved in some groups of integrals (cf equation (5)). Such a partial time ordering leads to a completely local, memory-free master equation [8]

$$\frac{\mathrm{d}P_n}{\mathrm{d}t}=\sum_{s=1}^{\infty}\sum_p\left(\frac{-\mathrm{i}}{\hbar}\right)^{s+1}\int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{s-1}}\mathrm{d}t_s K_{np}^{(s+1)}(t,t_1,\ldots,t_s)P_p(t) \tag{7}$$

with the matrix elements of the PTO cumulants coded as $K_{np}^{(s+1)}$.

Apart from the above equations, a large class of master equations with a restricted memory can also be derived. Their number depends on the number of terms retained in the sum over k in (4).

For one term ($\max(k)=1$), equation (5) reduces to the ordinary 'perturbation' series for the first-order cumulant $\Phi^{(1)}$. This case is represented by a single (first) column of table 1 with $\mu=\nu=\delta=\ldots=1$ and it is not interesting since $\Phi^{(1)}$ can always be eliminated for Hermitian interactions [4]. That is why we have neglected first-order cumulants from the very beginning and used this in the notation of (6) and (7). Clearly, all sums in (4) and (5) may be understood as starting from the value 2.

When $\max(k)=2$ in (4), two different time orderings result (the first two columns of table 1). They lead to equations (6) and (7) with $s=1$.

If in equation (4) $\max(k)=N$ (in general $N=\infty$), then there are $N-2$ additional ordering prescriptions of the type of (5) related to the values of $\mu=2,3,\ldots,k-1$ and $\nu=k$, $\delta=l$ etc. Now the values of μ, $\mu+\nu$, $\mu+\nu+\delta,\ldots$, are replaced by 2, $k+2$, $k+l+2,\ldots$, respectively or by the proper values from the other columns in table 1. All the choices have been called the modified partial time ordering prescriptions (MPTO) and one member of the family ($\mu=2$) yields the master equation [9]

$$\frac{\mathrm{d}P_n}{\mathrm{d}t}=\sum_{s=1}^{\infty}\sum_{p}\left(\frac{-\mathrm{i}}{\hbar}\right)^{s+1}\int^{t}\tilde{Q}_{np}^{(s+1)}(t,t_1)P_p(t_1)\,\mathrm{d}t_1 \tag{8}$$

where

$$\tilde{Q}_{np}^{(s+1)}(t,t_1)\equiv\int^{t_1}\mathrm{d}t_2\int^{t_2}\mathrm{d}t_3\ldots\int^{t_{s-1}}\mathrm{d}t_s Q_{np}^{(s+1)}(t,t_1,t_2,\ldots,t_s) \tag{9}$$

and

$$\tilde{Q}_{np}^{(2)}(t,t_1)=Q_{np}^{(2)}(t,t_1). \tag{10}$$

For $\mu=3$ the time argument of P_k in (8) would be t_2, for $\mu=4$ it would be t_3 and so on. Note that the memory is now partly taken into account and we expect to find the results of (8) to be between those of (6) and those of (7). This point is more fully elaborated in section 4.

Technical details of the above derivations can be found in [9] while the matrix elements of the MPTO cumulants $Q_{np}^{(s+1)}$ as well as TTO and PTO ones will be determined in section 3.

3. Cumulant matrix elements

Equations (6)-(8) are not useful in practice until matrix elements of the cumulant operators θ, K and Q are determined. This can be done by equating the expansion (5) with the series obtained from the expression (3). Such an approach allows one to easily find only the first few terms. However, for the TTO case a general formula can be derived. The result is presented here in the form of a theorem.

Theorem. Under the assumptions leading to (2) and (3) the matrix elements of the Nth-order TTO cumulant present in (6) are given by

$$\theta_{np}^{(N)}(t_1,t_2,\ldots,t_N)=\sum_{(i\neq j)}\sum_{(k\neq l)}\cdots\sum_{(u\neq v)}\sum_{(r\neq s)}\left\{\Lambda_{nn,ij}^{t_1}\Lambda_{ij,kl}^{t_2}\ldots\Lambda_{uv,rs}^{t_{N-1}}\Lambda_{rs,pp}^{t_N}\right\} \tag{11}$$

where, as in (2), $\{\ldots\}$ denotes an average over irrelevant variables, the sums are over pairs of different indices, and

$$\Lambda_{ab,cd}^{t}\equiv[H_{\mathrm{ri}}^{t}(t)]_{ac}\delta_{bd}-[H_{\mathrm{ri}}^{t}(t)]_{db}\delta_{ac}. \tag{12}$$

Besides, it follows immediately from (12) that for any N we have $\sum_p\theta_{np}^{(N)}=\sum_n\theta_{np}^{(N)}\equiv 0$.

In order to prove (11), let us write (2) in an equivalent form

$$P_n(t)=P_n(t_0)-\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t}\{(\Lambda^{t_1}\sigma^0)_{nn}\}\,\mathrm{d}t_1+\left(\frac{-\mathrm{i}}{\hbar}\right)^2\int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t_1}\mathrm{d}t_2\{\Lambda^{t_1}\Lambda^{t_2}\sigma^0)_{nn}\}+\ldots \tag{13}$$

where $\sigma^0 = \sigma(t_0)$ is assumed to be diagonal matrix and $\Lambda^t X = [H'_{ri}(t), X]$. Then, we can immediately observe that for the first-order term we get

$$\{(\Lambda^{t_1}\sigma^0)_{nn}\} = \sum_{ij} \{\Lambda^{t_1}_{nn,ij}\sigma^0_{ij}\} = 0 \tag{14a}$$

since

$$\Lambda^t_{aa,bb} \equiv 0 \tag{14b}$$

for any a and b. One of the higher-order terms gives, for example,

$$\begin{aligned}
&\{(\Lambda^{t_1}\Lambda^{t_2}\Lambda^{t_3}\Lambda^{t_4}\sigma^0)_{nn}\} \\
&\quad = \sum_{(i\neq j)} \{\Lambda^{t_1}_{nn,ij}(\Lambda^{t_2}\Lambda^{t_3}\Lambda^{t_4}\sigma^0)_{ij}\} \\
&\quad = \sum_{(i\neq j)} \sum_{kl} \{\Lambda^{t_1}_{nn,ij}\Lambda^{t_2}_{ij,kl}(\Lambda^{t_3}\Lambda^{t_4}\sigma^0)_{kl}\} \\
&\quad = \sum_{p} \sum_{(i\neq j)} \sum_{kl} \sum_{(r\neq s)} \{\Lambda^{t_1}_{nn,ij}\Lambda^{t_2}_{ij,kl}\Lambda^{t_3}_{kl,rs}\Lambda^{t_4}_{rs,pp}\}P_p(t_0).
\end{aligned} \tag{15}$$

Thus, it is not difficult to show that the Nth-order term of (13) can be written in the form

$$\begin{aligned}
\{M^{(N)}_{np}(t)\} = \left(\frac{-\mathrm{i}}{\hbar}\right)^N \int^t \mathrm{d}t_1 \int^{t_1} \mathrm{d}t_2 \ldots \int^{t_{N-1}} \mathrm{d}t_N \\
\times \sum_{(i\neq j)} \sum_{kl} \ldots \sum_{uv} \sum_{(r\neq s)} \{\Lambda^{t_1}_{nn,ij}\Lambda^{t_2}_{ij,kl} \ldots \Lambda^{t_{N-1}}_{uv,rs}\Lambda^{t_N}_{rs,pp}\}
\end{aligned} \tag{16}$$

and $\{M_{np}(t)\}$ of (2) is given by

$$\{M_{np}(t)\} = \sum_{N=2}^{\infty} \{M^{(N)}_{np}(t)\}. \tag{17}$$

Because of (14a), the contribution for $N = 1$ is zero.

The matrix elements of the TTO cumulants $\theta^{(N)}_{np}$ may now be determined by equating like powers of $\hbar$ for (5) and (16). For $N = 2$ and $N = 3$ the above theorem is obviously true, and we have:

$$\theta^{(2)}_{np}(t_1, t_2) = \sum_{(i\neq j)} \{\Lambda^{t_1}_{nn,ij}\Lambda^{t_2}_{ij,pp}\} \tag{18a}$$

$$\theta^{(3)}_{np}(t_1, t_2, t_3) = \sum_{(i\neq j)} \sum_{(k\neq l)} \{\Lambda^{t_1}_{nn,ij}\Lambda^{t_2}_{ij,kl}\Lambda^{t_3}_{kl,pp}\}. \tag{18b}$$

In the case of an arbitrary N, equations (5) and (16) lead to the relation

$$\theta^{(N)}_{np}(t_1, \ldots, t_N) + A^{(N)}_{np}(t_1, \ldots, t_N) = \sum_{(i\neq j)} \sum_{kl} \ldots \sum_{uv} \sum_{(r\neq s)} \{\Lambda^{t_1}_{nn,ij}\Lambda^{t_2}_{ij,kl} \ldots \Lambda^{t_{N-1}}_{uv,rs}\Lambda^{t_N}_{rs,pp}\} \tag{19}$$

where $A^{(N)}_{np}$ represents symbolically the np matrix element of the sum of products for cumulants of a suitable order.

For example, when $N = 5$ we have

$$A^{(5)}_{np}(t_1, \ldots, t_5) = [\theta^{(2)}(t_1, t_2)\theta^{(3)}(t_3, t_4, t_5)]_{np} + [\theta^{(3)}(t_1, t_2, t_3)\theta^{(2)}(t_4, t_5)]_{np} \tag{20}$$

since, as discussed earlier, the first-order cumulants can be eliminated. Now using in (20) the complete set of states of the operator H_r and bearing in mind the identity (14b), we get for $A^{(5)}_{np}$ a sum of two expressions like the RHS of (19) with four summations taken over $(i \neq j)$, $(k \neq l)$, $(r = s)$, $(u \neq v)$ and $(i \neq j)$, $(k = l)$, $(r \neq s)$, $(u \neq v)$. Subtracting the two contributions from the RHS of (19), we will obtain (11) for $N = 5$.

A generalisation to arbitrary N can be done in a similar way. It is, however, too lengthy to be presented here. Instead of that we shall show another, much simpler, idea for proving (11).

We start from the equation $\partial\sigma/\partial t = -(\mathrm{i}/\hbar)[H'_{\mathrm{ri}}, \sigma]$, the solution of which is (1). The equation for σ can be written in the tetradic form both for diagonal as well as non-diagonal matrix elements. If that for the diagonal elements is additionally ensemble averaged, then:

$$\frac{\mathrm{d}\sigma_{ij}}{\mathrm{d}t} = \frac{-\mathrm{i}}{\hbar} \sum_{kl} \Lambda^{t}_{ij,kl}\sigma_{kl}(t) \tag{21a}$$

$$\frac{\mathrm{d}P_n}{\mathrm{d}t} = \frac{-\mathrm{i}}{\hbar} \sum_{(i\neq j)} \{\Lambda'_{nn,ij}\sigma_{ij}(t)\}. \tag{21b}$$

In the following, the formal solution of (21a), with the initial density matrix taken to be diagonal, is repeatedly inserted into (21b). Extracting each time the diagonal matrix elements of σ, we get after an infinite number of such manipulations an equation which, upon being compared with (6), leads again to the result (11). Such a procedure has been shown to be convergent for a model problem [10].

We were not able to derive general relations like (11) for cumulants of other kinds. That is not, however, an inconvenience since (i) the TTO-like master equations give much better results than the other equations (see section 4) and (ii) low-order cumulants of the remaining kinds may also be determined from (11). The latter statement can be proved when low-order terms of expansion (5) for the TTO, PTO and MPTO ($\mu = 2$) time orderings are compared. This shows that $\boldsymbol{\theta}^{(i)} = \mathbf{Q}^{(i)} = \mathbf{K}^{(i)}$ for $i = 2$, 3 and $\boldsymbol{\theta}^{(4)} = \mathbf{Q}^{(4)} \neq \mathbf{K}^{(4)}$ whereas the higher-order cumulants are all different.

4. Applications to a model problem

In this section we shall report some results obtained from integrations of (6), (7) and (8) for the model Hamiltonian

$$H'_{\mathrm{ri}}(t) = G(t)(a^{+}b^{-} + a^{-}b^{+}). \tag{22}$$

It describes a collinear collision of two diatomic molecules treated as harmonic oscillators [11], where $a^{\pm}$ and $b^{\pm}$ are boson operators acting in the space of oscillator states of the first and second molecule, respectively. The analytical form of the function $G(t)$ depends on the assumed form of a classical trajectory of the relative motion of the molecules.

In this semiclassical approximation the quantum ensemble average of (11) may be replaced by a classical one which involves delta functions along the classical trajectory. $P_n(t)$ should not be understood as $P_{nN}(t)$, which is a probability distribution for one oscillator to be in the state $|n\rangle$ and the other one to be in the state $|N\rangle$. The product $|n\rangle|N\rangle \equiv |n, N\rangle$ is an eigenstate of the Hamiltonian $H_{\mathrm{r}} = \hbar\omega(a^{+}a^{-} + \frac{1}{2}) + \hbar\omega(b^{+}b^{-} + \frac{1}{2})$.

It has been shown [12] that for the model (22), master equations of any order and any kind have solutions of the general form

$$P_{k\to n}(\beta, t) = (-1)^{n+k} \sum_{s=0}^{\beta} h(s, t)C(\beta, k, s)C(\beta, n, s). \tag{23}$$

In the formula $\beta = \mathrm{I} + \mathrm{i} = \mathrm{F} + \mathrm{f} = 0, 1, 2, \ldots$, and is the sum of initial or final quantum numbers of both oscillators. The symbol $C(\beta, j, s)$ stands for the Clebsch-Gordan coefficient

$$C(\beta, j, s) = \left(\frac{\beta}{2}, \frac{\beta}{2}, \frac{\beta}{2} - j, \frac{-\beta}{2} + j \middle| s, 0\right) \tag{24}$$

which obeys the identity [13]

$$f(j)C(\beta, j+1, s) + [f(j) + f(j-1)]C(\beta, j, s) + f(j-1)C(\beta, j-1, s) = s(s+1)C(\beta, j, s) \tag{25}$$

where

$$f(j) = (j+1)\beta - j^2 - j. \tag{26}$$

An analytic form of the function $h(s, t)$ in (23) depends on the order and the kind of the master equation under consideration.

In order to see the differences in the solutions of (6), (7) and (8), they have been solved up to the fourth-order cumulants. This corresponds to the values of $s = 1$ and $s = 3$ in the equations, since for the model (22) the third-order cumulants ($s = 2$) are zero.

The functions $h(s, t)$ in each of the three master equations can be found in the following way. First we determine the matrix elements of the second- and fourth-order cumulants for the TTO, PTO and MPTO cases in the basis of $|n, N\rangle$ states. Introducing then the parameter β and postulating solutions in the form of (23), we get with the help of (25) the unknown functions $h(s, t)$. Such a method has already been described in detail in [10, 12] and here we only present the final solutions.

The TTO master equation (6) leads to the function

$$h^{\mathrm{T}}(s, \xi) = \frac{(D^+)^2 \cos(D^+\xi) + (D^-)^2 \cosh(D^-\xi)}{(D^-)^2 + (D^+)^2} \tag{27}$$

where

$$D^{\pm} = [\pm s(s+1) + \{s(s+1)[3s(s+1) - 4]\}^{1/2}]^{1/2} \tag{28}$$

$$\xi(t) = \frac{1}{\hbar} \int_{-\infty}^{t} G(t_1)\, \mathrm{d}t_1. \tag{29}$$

In the PTO case (equation (7)), we get

$$h^{\mathrm{P}}(s, \xi) = \exp\{-s(s+1)[\xi^2 + (\xi^4/12)(7s^2 + 7s - 2)]\}. \tag{30}$$

The last case, the MPTO equation (8) yields

$$h^{\mathrm{M}}(s, \xi) = \exp\left(\frac{-b}{2}\xi^2\right) F\left(\frac{b-a}{4b}, \frac{1}{2}, b\xi^2\right) \tag{31}$$

where

$$a = 2s(s+1) \tag{32a}$$

$$b = \{s(s+1)[s(s+1) - 2]\}^{1/2} \tag{32b}$$

and $F(\alpha, \beta, x)$ is a Kummer function or degenerate hypergeometric function [14].

For comparison, the exact solution for the model (22) corresponding to the infinite-order TTO master equation (6) can also be found [10]

$$h^{E}(s, \xi) = P_s(\cos 2\xi) \tag{33}$$

with the P_s being the Legendre polynomial of order s.

The functions given in (27), (30), (31) and (33) are plotted for $s = 2$ in figure 1 as a function of ξ. The latter quantity can be considered as an average energy transferred during a collision. At low values of ξ all four approaches lead to very similar results indistinguishable in drawings. When the value of ξ is increasing, the solution of the master equation with no memory taken into account (P) tends to zero and fails for $\xi > 0.45$. Making allowances for memory as in (8), even if only partially, extends the applicability of the approximate theory (M) as compared with the exact one. As soon as the memory is completely considered, as in (6), the obtained results (T) are closer to the exact (E) ones than the other results. Moreover, they reflect the correct behaviour in the whole range of ξ. A similar tendency has also been observed for higher values of s not presented here.

To sum up: from among the three types of master equations, that given by (6) is highly recommended. For the equation to be useful in practice, a general formula (equation (11)) for the TTO matrix elements has been derived and applied to a simple model. It is the only known model for which exact solutions of non-local master equations can be found in a closed analytical form.

As we have shown at the end of section 3 the formula (11) can also be used for the low-order PTO and MPTO cumulant matrix elements. As a result, the corresponding master equations can be written without any effort. In this work not only all possible time ordering prescriptions have been systematised but a detailed comparison between the predictions of different master equations has also been made.

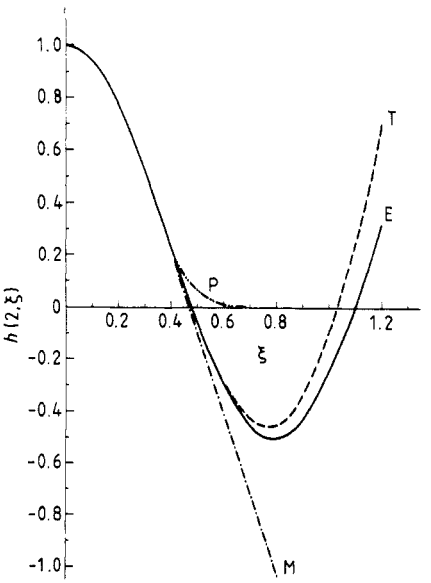

Figure 1. The plot of the function $h(2, \xi)$ for the modified partial (M), total (T) and partial (P) time ordering master equations. The exact solution presented for comparison is denoted by the letter E.

The results of master equations of the three types discussed here (equations (6)-(8)) are exact in principle provided the appropriate terms are evaluated to infinite order. This follows from the fact that the expansion (5) is equated to all terms in the expansion of (3). Equations (6)-(8) yield identical results for $s = 1$ in the Markovian limit. However, in general, when the next terms in s are taken into account and the Markovian assumption does not hold, the three equations predict a very different behaviour. This is clearly shown in figure 1 for a simple model Hamiltonian.

Though the totally non-Markovian master equation (6) is recommended for exact calculations, this does not mean that equations of the other types are useless. The 'standard' cumulant expansion, first introduced by Kubo [2], corresponding to what is known as the PTO approach, has been found to be useful for time domain analysis [5]. No memory is involved in this case. In contrast, the TTO cumulant method, introduced in [5], seems to be more convenient for the frequency domain when one wants to calculate, e.g., spectra or lineshapes [3, 6]. Now, the master equation is completely non-local with the memory effects totally taken into account.

In between the two extreme possibilities, a large class of MPTO master equations with a restricted memory can be found. They are much simpler to use than TTO equations and can lead to better results than PTO ones. The comparison made in this work gives a contribution for better understanding the range of validity and limitations of these methods.

Acknowledgment

This work has been supported in part by the Polish Ministry of National Education (Project CPBP 01.06).

References

[1] Haake F 1973 *Springer Tracts in Modern Physics* **66** (Berlin: Springer)
Agarwal G S 1973 *Progress in Optics* **11** (Amsterdam: North-Holland)
Van Kampen N G 1976 *Phys. Rep.* **24C** 171
Gardiner C W 1985 *Handbook of Stochastic Methods* (Berlin: Springer) (2nd edn)
[2] Kubo R 1962 *J. Phys. Soc. Japan* **17** 1100; 1962 *J. Math. Phys.* **4** 174
[3] Mukamel S, Oppenheim I and Ross J 1978 *Phys. Rev.* A **17** 1988
Mukamel S 1979 *Chem. Phys.* **37** 33
[4] Freed J H 1968 *J. Chem. Phys.* **49** 376
[5] Yoon B, Deutch J M and Freed J H 1975 *J. Chem. Phys.* **62** 4687
[6] Faid K and Fox R F 1986 *Phys. Rev.* A **34** 4286
[7] Schatz G C 1977 *J. Chem. Phys.* **66** 5220
[8] Schatz G C 1978 *Chem. Phys. Lett.* **58** 368
[9] Makowski A J 1988 *J. Phys. A: Math. Gen.* **21** L789
[10] Dembinski S T and Makowski A J 1984 *Chem. Phys.* **90** 109
[11] Kelley J D 1972 *J. Chem. Phys.* **56** 6108
[12] Makowski A J and Orlikowski T 1982 *Chem. Phys.* **64** 231
[13] Makowski A J 1982 *Chem. Phys.* **68** 317
[14] Abramowitz M and Stegun I A 1964 *Handbook of Mathematical Functions* (National Bureau of Standards) ch 13