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LETTER TO THE EDITOR

Time ordering of a cumulant expansion and master equations

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Abstract. Based on cumulant expansions a new class of master equations with a restricted memory is derived. The equations generalise local master equations based on the partial time-ordering prescription. They are simpler to use than completely non-local equations derived with the help of the total time-ordering prescription.

Following the idea of Kubo [1] many applications of cumulant expansions have been made in the past [2]. Some of the most representative examples are provided by works on molecular [3] and spin [4, 5] relaxations, stochastic collision theory [6, 7] and the theory of lineshapes [8].

Starting with the Liouville equation and using cumulant expansions two different equations of motion (master equations) for the reduced density operator have been derived. The form of the master equations depends on the chosen prescription for the time ordering of the cumulant expansion (see below). Two specific choices are known in the literature. One of them, referred to as a partial time ordering (PTO) [1, 4], leads to an equation local in time. The second choice, called a total time ordering (TTO) [5], produces a non-local master equation exactly equivalent to that derived with the projection operator technique.

The aim of this letter is to systematise possible ways of the time prescriptions and to derive a master equation of a new type based on a PTO-like ordering. It will also be shown that the non-locality of a master equation, usually attributed to the TTO prescription, can also be achieved with the help of a modified PTO approach. Contrary to most approaches we will not derive equations of motion for the reduced density operator itself but rather for its diagonal elements.

Let us now consider a dynamical system, for example two colliding molecules. The Liouville equation $\partial\rho/\partial t = -\mathrm{i}L\rho$, where $L\rho = (1/\hbar)\,[H, \rho]$ and H is the complete Hamiltonian of the system, can be reduced so as to eliminate some irrelevant quantities. The procedures of this kind are well known and will not be discussed here. To become more specific we refer the reader to one of them given in [6] which, for a non-reactive collision of two molecules, leads to the relation

$$P_n(t) = \sum_k \{M_{nk}(t)\} P_k(t_0) \tag{1}$$

where

$$M_{nk}(t) = \left| \left\langle n \middle| T \exp\left(\frac{-\mathrm{i}}{\hbar} \int_{t_0}^{t} H_{\mathrm{ri}}(t_1)\, \mathrm{d}t_1 \right) \middle| k \right\rangle \right|^2 . \tag{2}$$

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The symbol $P_n(t)$ stands for the reduced probability of, for example, internal state n and H_{ri} is an interaction between relevant and irrelevant variables and $\{\ \}$ is an average over irrelevant variables [6]. Equation (1) has been derived assuming weak correlations between the variables and uncorrelated initial conditions. In the following, instead of (1) its matrix form

$$\boldsymbol{P}(t) = \boldsymbol{M}(t)\boldsymbol{P}(t_0) \tag{3}$$

and the time derivative

$$\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t} = \frac{\mathrm{d}\boldsymbol{M}}{\mathrm{d}t}\boldsymbol{P}(t_0) \tag{4}$$

will be used.

In the cumulant method, the matrix $\boldsymbol{M}(t)$ can be re-expressed in terms of sums of cumulants $\boldsymbol{\Phi}^{(k)}$:

$$\boldsymbol{M}(t) = \exp_{\mathrm{o}}\left[\sum_k \left(\frac{-\mathrm{i}}{\hbar}\right)^k \int^t \mathrm{d}t_1 \int^{t_1} \mathrm{d}t_2 \ldots \int^{t_{k-1}} \mathrm{d}t_k\, \boldsymbol{\Phi}^{(k)}(t_1, t_2, \ldots, t_k)\right]. \tag{5}$$

The sum over k in (5) runs, in general, from one to infinity. The cumulants $\boldsymbol{\Phi}^{(k)}$ are determined by equating terms of the same order in expansions of (2) and (5). It can be easily shown that $\boldsymbol{\Phi}^{(1)} \equiv \mathbf{0}$ when the interaction operator is Hermitian. That is why we neglect the first-order cumulants from the very beginning, assuming that k starts from the value of 2. The subscript 'o' of exp denotes the appropriate ordering prescription, the choice of which becomes a crucial point.

To see that, the expansion of (5) is proposed in the form:

$$\begin{aligned}
\boldsymbol{M}(t) = \boldsymbol{I} &+ \sum_k \left(\frac{-\mathrm{i}}{\hbar}\right)^k \int^t \mathrm{d}t_1 \int^{t_1} \mathrm{d}t_2 \ldots \int^{t_{k-1}} \mathrm{d}t_k\, \boldsymbol{\Phi}^{(k)}(t_1, t_2, \ldots, t_k) \\
&+ \sum_k \sum_l \left(\frac{-\mathrm{i}}{\hbar}\right)^{k+l} \int^t \mathrm{d}t_1 \int^{t_1} \mathrm{d}t_2 \ldots \int^{t_{k-1}} \mathrm{d}t_k\, \boldsymbol{\Phi}^{(k)}(t_1, t_2, \ldots, t_k) \\
&\times \int^{t_\mu} \mathrm{d}t_{k+1} \int^{t_{k+1}} \mathrm{d}t_{k+2} \ldots \int^{t_{k+1-1}} \mathrm{d}t_{k+l}\, \boldsymbol{\Phi}^{(l)}(t_{k+1}, t_{k+2}, \ldots, t_{k+l}) \\
&+ \sum_k \sum_l \sum_s \left(\frac{-\mathrm{i}}{\hbar}\right)^{k+l+s} \int^t \mathrm{d}t_1 \int^{t_1} \mathrm{d}t_2 \ldots \int^{t_{k-1}} \mathrm{d}t_k\, \boldsymbol{\Phi}^{(k)}(t_1, t_2, \ldots, t_k) \\
&\times \int^{t_\mu} \mathrm{d}t_{k+1} \int^{t_{k+1}} \mathrm{d}t_{k+2} \ldots \int^{t_{k+l-1}} \mathrm{d}t_{k+l}\, \boldsymbol{\Phi}^{(l)}(t_{k+1}, t_{k+2}, \ldots, t_{k+l}) \\
&\times \int^{t_{\mu+\nu}} \mathrm{d}t_{k+l+1} \int^{t_{k+l+1}} \mathrm{d}t_{k+l+2} \ldots \\
&\times \int^{t_{k+l+s-1}} \mathrm{d}t_{k+l+s}\, \boldsymbol{\Phi}^{(s)}(t_{k+l+1}, t_{k+l+2}, \ldots, t_{k+l+s}) + \ldots .
\end{aligned} \tag{6}$$

Different time orderings manifest themselves in different proper placing of the upper limits of integrations t_μ, $t_{\mu+\nu}$, $t_{\mu+\nu+\delta}$ and so on. The above expansion clearly shows the rule. The lower limits of all integrals are the same and represent the initial time.

We shall now distinguish three cases.

(i) Setting in (6) $\mu = k$, $\nu = 1$, $\delta = s, \ldots$, we get what is called the TTO expansion, since all the upper limits are completely ordered in a chronological way. This case

has been described in [5]. Differentiating $\boldsymbol{M}(t)$ with respect to time [5] and then using (4) and (3) we get the generalised non-local master equation

$$\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t}=\sum_{s=1}^{\infty}\left(\frac{-\mathrm{i}}{\hbar}\right)^{s+1}\int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{s-1}}\mathrm{d}t_s\,\boldsymbol{\theta}^{(s+1)}(t,t_1,\ldots,t_s)\boldsymbol{P}(t_s) \tag{7}$$

with the TTO cumulants denoted by $\boldsymbol{\theta}^{(s+1)}$.

(ii) Setting now $\mu=1$ and $\nu=k$, $\delta=l,\ldots,$ in (6) the PTO expansion [1, 4, 5, 7] is defined. In this case the chronological order of upper limits in time integrals is only guaranteed for particular groups of integrals. Again, taking the time derivative of $\boldsymbol{M}(t)$ and using (4) and (3) we get

$$\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t}=\sum_{s=1}^{\infty}\left(\frac{-\mathrm{i}}{\hbar}\right)^{s+1}\int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{s-1}}\mathrm{d}t_s\,\boldsymbol{K}^{(s+1)}(t,t_1,\ldots,t_s)\cdot\boldsymbol{P}(t). \tag{8}$$

This is clearly a completely local (memoryless) master equation with the PTO cumulants denoted by $\boldsymbol{K}^{(s+1)}$.

(iii) We suggest here a third class of time orderings leading to master equations with a restricted memory. This class is obtained when the value of μ in the expansion (6) is in between one and k with $\nu=k$, $\delta=l$ and so on. We shall call this expansion the modified partial time-ordering (MPTO) prescription or the PTO expansion with memory. One of the cases, for $\mu=2$, can be of particular importance. To find the corresponding master equation it is necessary to calculate $\mathrm{d}\boldsymbol{M}/\mathrm{d}t$ for this case. The simplest way to do that is as follows. First, we expand the sums over k in (6). Then, we calculate the time derivatives of the terms with $k=2,3,\ldots$. Next, we gather terms with $k=2$ and observe that they are multiplied by a common factor of

$$(-\mathrm{i}/\hbar)^2\int^{t}\boldsymbol{Q}^{(2)}(t,t_1)\,\mathrm{d}t_1.$$

All the terms with $k=3$ have the factor

$$(-\mathrm{i}/\hbar)^3\int^{t}\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\,\boldsymbol{Q}^{(3)}(t,t_1,t_2)$$

and so on. Each of the factors multiplies a series which represents $\boldsymbol{M}(t_1)$. In this way we finally obtain

$$\frac{\mathrm{d}\boldsymbol{M}}{\mathrm{d}t}=\sum_{s=1}^{\infty}\left(\frac{-\mathrm{i}}{\hbar}\right)^{s+1}\int^{t}\boldsymbol{M}(t_1)\,\mathrm{d}t_1\int^{t_1}\mathrm{d}t_2\ldots\int^{t_{s-1}}\mathrm{d}t_s\,\boldsymbol{Q}^{(s+1)}(t,t_1,\ldots,t_s) \tag{9}$$

where $\boldsymbol{Q}^{(s+1)}$ denote cumulants for the case under consideration. Now, using (3), (4) and (9) and denoting

$$\tilde{\boldsymbol{Q}}^{(s+1)}(t,t_1)\equiv\int^{t_1}\mathrm{d}t_2\int^{t_2}\mathrm{d}t_3\ldots\int^{t_{s-1}}\mathrm{d}t_s\,\boldsymbol{Q}^{(s+1)}(t,t_1,\ldots,t_s) \tag{10}$$

with $\tilde{\boldsymbol{Q}}^{(2)}(t,t_1)\equiv\boldsymbol{Q}^{(2)}(t,t_1)$ the following master equation is derived:

$$\frac{\mathrm{d}\boldsymbol{P}}{\mathrm{d}t}=\sum_{s=1}^{\infty}\left(\frac{-\mathrm{i}}{\hbar}\right)^{s+1}\int^{t}\tilde{\boldsymbol{Q}}^{(s+1)}(t,t_1)\boldsymbol{P}(t_1)\,\mathrm{d}t_1. \tag{11}$$

For $\mu=3$ in (6) the argument of $\boldsymbol{M}$ in (9) would be t_2, for $\mu=4$ it would be t_3 and so on.

An analysis of the expansion (6) for the three classes of orderings shows that $\boldsymbol{\theta}^{(i)} = \boldsymbol{Q}^{(i)} = \boldsymbol{K}^{(i)}$ for $i = 2, 3$ and $\boldsymbol{\theta}^{(4)} = \boldsymbol{Q}^{(4)} \neq \boldsymbol{K}^{(4)}$ whereas the higher-order cumulants are all different. Thus our (11), in the lowest-order case ($s = 1$), is the same as (7) and differs from (8). For $s = 2$ all the three master equations lead to a completely different time evolution with the same definition for the three kinds of cumulants.

If an infinite number of cumulants are taken into account the choice of the method of time prescription in (6) is not important. This follows from the fact that cumulants are defined by equating the expansion (6) with all terms of expansion of (2).

Note that the number of time prescriptions of the same type as (6) depends on the number of terms retained in the sum over k in (5). For one term ($k = 2$) there exist two time orderings: one of them is TTO and another one is PTO. For two terms ($k = 2, 3$) there are three possibilities: TTO, PTO and MPTO, corresponding to $\mu = 2$ in (6). When the sum over k in (5) contains N terms then there exist $N + 1$ different time orderings with $N - 1$ MPTO prescriptions. This exploits all the interesting cases based on the expansion (6).

Convergence of the solutions of the Markovian master equation (8) for $s = 1, 2, \ldots, \infty$ has been studied in [7] for a simple collision model. In another study [9] with a different collision model the same problem has been studied for a non-Markovian master equation like (7). A similar analysis of our (11), which can be called a semi-Markov equation [10], will be given elsewhere.

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