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Relaxation processes in systems strongly coupled to a harmonic bath

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The simulation of nonlinear optical experiments in the condensed phase often requires including relaxation between different states of matter due to interaction with an external bath. This is commonly done using second-order Redfield or Lindblad equations. Here, we derive closed expressions for relaxation equations to any order in the coupling to a harmonic bath. This is done using a compact superoperator notation combined with reduced equations of motions based on Time Convolutionless theory (TCL), partial ordering prescription.

Keywords: Time Convolutionless theory; Redfield equations; relaxation

1. Introduction

Nonlinear optical techniques are widely used to monitor the electronic and vibrational dynamics in diverse systems such as photosynthetic pigments, coupled nanostructures or hybrid nanomaterials [1–3]. Theoretical simulations of these experiments require a proper description of relaxation and dephasing processes. The relaxation is commonly described by assuming a linear coupling of the electronic system to a harmonic bath and deriving Redfield equations to second order in the system–bath coupling, or their non-Markovian extension. However, if the system–bath interaction reaches a certain strength, the second-order Redfield equation predicts unphysical evolution and the inclusion of higher order contributions to the relaxation kernel becomes necessary. The resulting equations are lengthy and hard to use. Hereby utilizing the superoperator representation and algebra introduced in [4–7], we derive equations of motion for the relaxation of the density matrix to any order of the system–bath coupling. A compact form for the relaxation kernel, recast in terms of bath response functions, gives insights into the physical properties of the relaxation processes.

The paper is organized as follows. First, we give a brief overview of the superoperator representation used in this paper. We then present a model Hamiltonian for a system coupled to a harmonic bath. We describe the construction of Time Convolutionless theory (TCL) equations together with van Kampen's rules [8,9] for ordered cumulants. The TCL results are given to any order in the system–bath coupling.

2. The +/– representation of superoperators

We assume a system coupled to a bath and described by the Hamiltonian $H = H_0 + H'$, where H_0 represents the isolated system and bath and H' is their coupling. A quantum mechanical system is described by its density matrix ρ , whose time evolution in the interaction picture is given by the Liouville–von Neumann equation $\partial_t \rho(t) = \frac{i}{\hbar} [\rho, H'(t)]$. Here $H'(t) = e^{iH_0 t} H'(0) e^{-iH_0 t}$. The Liouville space is a direct product space of system and bath space. For any operator A on this product system and bath Hilbert space, we define the following superoperators by their action on an arbitrary ordinary (Hilbert space) operator F :

$$A_L F := A F \quad A_R F := F A, \quad (1)$$

as the subscript implies the operator A acts either to the left or to the right side of the operator F . An alternative (+/–) representation of the superoperators can be formulated using the following transformation:

$$A_+ := \frac{1}{2}(A_L + A_R) \quad A_- := A_L - A_R. \quad (2)$$

This representation allows us to derive more compact expressions in many applications. The Liouville–von Neumann equation now reads $\partial_t \rho = -\frac{i}{\hbar} [H'(t)]_- \rho$. In the following derivations we will use some algebraic properties of superoperators. A function of the superoperator is defined as follows:

$$[f(A)]_- := f(A_L) - f(A_R) \quad 2[f(A)]_+ := f(A_L) + f(A_R). \quad (3)$$

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From these definitions it follows immediately that, for commuting operators A and B , we have:

$$(AB)_- = A_+B_- + A_-B_+ \quad (AB)_+ = A_+B_+ + A_-B_- \quad (4)$$

This is the case, for example, if one of the operators acts only on the bath part and the other on the system part of the product space.

3. The cumulant expansion

We introduce a set of operators S^i that constitute an orthogonal basis of the Liouville space of the system. The basis S^i is chosen to be diagonal in the energy eigenstates of the system, so that in the interaction picture $S^k(t) = e^{i\varepsilon_k t} S^k(0)$ holds. Note, that ε_i represents the energy difference between the two Hilbert space vectors forming the Liouville space vector S^i . The interaction between the system and bath contains products of system and bath operators.

$$H'(t) = \sum_i A_i S^i(t) \otimes F^i(t). \quad (5)$$

We start with the Liouville–von Neumann equation in the interaction picture:

$$\partial_t \rho(t) = -\frac{i}{\hbar} H'_-(t) \rho(t). \quad (6)$$

We are interested in the reduced system density matrix $\rho_S = \text{tr}_B(\rho)$. All system observables are only connected with ρ_S . Following Nakajima and Zwanzig [10,11], we introduce the projection operator $\mathcal{P}\rho = \text{tr}_B(\rho) \otimes \rho_B \equiv \rho_S \otimes \rho_B$, where ρ_B is the canonical density operator of the bath. $\mathcal{P}\rho$ contains effectively only information on ρ_S , since ρ_B is known. We now wish to bring the equation for $\mathcal{P}\rho$ into the convolutionless form introduced by [12–16], which has been applied to many systems [17,18] and is still subject to improvements [19–22]. Equation (6) can be solved formally, which leads to $\rho(t) = T \exp(-\frac{i}{\hbar} \int_{t_0}^t dt' H'_-(t')) \rho(t_0)$, T is the time ordering operator, ordering super operators with increasing time arguments from right to left. We assume that initially $\rho(t_0) = \mathcal{P}\rho(t_0)$. Using these definitions the reduced system density matrix is given by:

$$\mathcal{P}\rho(t) = \mathcal{P} T \exp\left(-\frac{i}{\hbar} \int_{t_0}^t dt' H'_-(t')\right) \mathcal{P}\rho(t_0). \quad (7)$$

This formula can be inverted $\mathcal{P}\rho(t_0) = (\mathcal{P} T \exp(-\frac{i}{\hbar} \int_{t_0}^t dt' H'_-(t')) \mathcal{P})^{-1} \mathcal{P}\rho(t)$.

We can take the time derivative $\partial_t \mathcal{P}\rho(t) = \frac{i}{\hbar} \mathcal{P} H'_-(t) (T \exp(-\frac{i}{\hbar} \int_{t_0}^t dt' H'_-(t'))) \mathcal{P}\rho(t_0)$. Combining these equations leads to:

$$\partial_t \mathcal{P}\rho(t) = \mathcal{K}(t) \mathcal{P}\rho(t), \quad (8)$$

where

$$\mathcal{K}(t) = \mathcal{P} \frac{i}{\hbar} H'_-(t) T \exp\left(-\frac{i}{\hbar} \int_{t_0}^t dt' H'_-(t')\right) \times \mathcal{P} \left(\mathcal{P} T \exp\left(-\frac{i}{\hbar} \int_{t_0}^t dt' H'_-(t')\right) \mathcal{P} \right)^{-1}. \quad (9)$$

By rewriting the expression $(\mathcal{P} T \exp(-\frac{i}{\hbar} \int_{t_0}^t dt' H'_-(t')) \mathcal{P})^{-1}$ in to the form $(1 + \dots)^{-1}$, we can apply a Neumann series and then use a Taylor series to expand this expression in orders of the system bath coupling:

$$\mathcal{K}(t) = \sum_n \mathcal{K}_n(t). \quad (10)$$

Equation (10) is known as the cumulant expansion, and \mathcal{K}_n is the n th cumulant.

4. The second-order Redfield equations

To demonstrate how the cumulant expansion works, we start by evaluating \mathcal{K}_2 using the $+/-$ representation. We assume here $\langle H'(t) \rangle = 0$ and thus \mathcal{K}_1 vanishes. Using Equation (4), the second-order result reads:

$$\mathcal{K}_2(t) = -\frac{1}{\hbar^2} \sum_{mk} A_m A_k \int_{t_0}^t dt_1 \cdot [\langle T F_+^m(t) F_-^k(t_1) \rangle T S_-^m(t) S_+^k(t_1) + \langle T F_+^m(t) F_+^k(t_1) \rangle T S_-^m(t) S_-^k(t_1)]. \quad (11)$$

The bath correlation functions appearing in the two contributions are connected by the fluctuation dissipation theorem (illustrated later by using the Markovian approximation). The $-+$ and $--$ bath correlation functions with $+ -$ and $++$ are connected to system operators with the opposite indices. Since the system part is still an operator and not under a trace, having a $-$ operator at the left-hand side would not cause the term to vanish. The opposite is true for a system $-$ operator at the left, a $+$ system operator will lead to unphysical results. Since only the $-$ operator on the left ensures the trace conservation in an equation of motion:

$$0 = \partial_t \text{tr}(\mathcal{P}\rho) = \text{tr}(S_- B \mathcal{P}\rho) = 0, \quad (12)$$

where B is any superoperator. A system $+$ operator would violate the trace conservation. A system $+$ operator does not appear at the left side since $\langle T F_-^n(t) A \rangle = 0$.

An often applied Markovian approximation eliminates in second order all aspects of time ordering and thus the result is the same for TCL theory or Nakijma-Zwanzig treatments, which utilize a different scheme for time ordering.

To apply Markovian approximation, the integration variable in Equation (11) is substituted with $\tau = t - t_1$ and the upper integration boundary is taken to infinity to remove memory effects, and reads:

$$\partial_t \mathcal{P} \rho(t) = \mathcal{K}'_2(t) \mathcal{P} \rho(t) \quad (13)$$

with

$$\begin{aligned} \mathcal{K}'_2(t) = & -\frac{i}{\hbar^2 2\pi} \sum_{mk} A_m A_k e^{i(\varepsilon_m + \varepsilon_k)t} \int d\omega \frac{1}{\omega - \varepsilon_k - i\eta} \\ & \times [F_{+-}^{mk}(\omega) S_-^m S_+^k + F_{++}^{mk}(\omega) S_-^m S_-^k] \end{aligned} \quad (14)$$

with $F_{+-}^{ij}(\omega) = [C_{ij}(\omega) - C_{ij}(-\omega)]$ and $F_{++}^{nl}(\omega) = [C_{ij}(\omega) \coth(\frac{\beta\hbar\omega}{2}) + C_{ij}(-\omega) \coth(-\beta\hbar\omega/2)]$ [5]. Transformed to the Schrödinger picture, we finally get:

$$\partial_t \mathcal{P} \rho(t) = -\frac{i}{\hbar} [H_0]_- \mathcal{P} \rho(t) + \tilde{\mathcal{K}}'_2 \mathcal{P} \rho(t) \quad (15)$$

with

$$\begin{aligned} \tilde{\mathcal{K}}'_2 = & -\frac{i}{\hbar^2 2\pi} \sum_{mk} A_m A_k \int d\omega \frac{1}{\omega - \varepsilon_k - i\eta} \\ & \times [F_{+-}^{mk}(\omega) S_-^m S_+^k + F_{++}^{mk}(\omega) S_-^m S_-^k]. \end{aligned} \quad (16)$$

The bath correlation functions read:

$$\langle TF_+^n(t) F_-^l(0) \rangle = \theta(t) \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} F_{+-}^{nl}(\omega) \quad (17)$$

$$\langle TF_+^n(t) F_+^l(0) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{i\omega t} F_{++}^{nl}(\omega) \quad (18)$$

with $S^k(t) = e^{i\varepsilon_k t} S^k(0)$. The spectral densities $C_{ij}(\omega)$ are the only necessary input regarding the system-bath coupling. The Fourier transforms of the two bath correlation functions $\langle TF_+^n(t) F_-^l(0) \rangle$ and $\langle TF_+^n(t) F_+^l(0) \rangle$ are connected by a Kramers–Kronig relation:

$$F_{+-}^{nl}(\omega) = 2 \frac{1}{2\pi} \int d\omega' \frac{1}{\omega - \omega' - i\eta} \frac{F_{++}^{nl}(\omega')}{\coth(\beta\hbar\omega'/2)}. \quad (19)$$

By contour integration this gives the fluctuation dissipation relation:

$$F_{++}^{nl}(\omega) = \coth(\beta\hbar\omega/2) \text{Im}(F_{+-}^{nl}(\omega)). \quad (20)$$

The second-order relaxation equations in the Markovian approximation are known as Redfield equations. The $+, -$ representation results in more compact formal expressions than the standard tetradic expressions.

5. The fourth-order relaxation Kernel

Hereafter, we assume linear coupling to a harmonic bath. F^i in Equation (5) is assumed to be $F^i(t) =$

$\sum_{\alpha} B_{i\alpha} Q_{\alpha}(t)$. Here Q_{α} are canonical bosonic bath variables $[Q_{\alpha}, P_{\beta}]_- = i\hbar \delta_{\alpha\beta}$. A harmonic bath means that the Hamiltonian for the canonical baths is quadratic in Q_{α} . All odd moments of the Hamiltonians vanish: $\text{tr}(H'(t_1)H'(t_2)\dots H'(t_{2n+1})\rho_B) = 0$. Higher order equations can be evaluated using Wick's theorem [5]:

$$\begin{aligned} & \langle TF_{\sigma_1}^{n_1}(t_1) \dots F_{\sigma_N}^{n_N}(t_N) \rangle \\ & = \sum_P \langle TF_{\sigma_a}^{n_a}(t_a) F_{\sigma_b}^{n_b}(t_b) \dots TF_{\sigma_p}^{n_p}(t_p) F_{\sigma_q}^{n_q}(t_q) \rangle \end{aligned} \quad (21)$$

where $n_a, \sigma_a \dots n_q, \sigma_q$ is a permutation of $n_1, \sigma_1 \dots n_N, \sigma_N$ summing over all possible permutations [5] and indices $\sigma_i = +$ or $-$.

Only a few treatments are known where these equations are actually evaluated up to the next (fourth) order [9]. Using Equation (9), the fourth-order cumulant is:

$$\begin{aligned} \mathcal{K}_4(t) = & \left(-\frac{i}{\hbar}\right)^4 \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \int_{t_0}^t dt_3 \\ & \times \left(\frac{1}{3!} \mathcal{P} T H_-(t) H_-(t_1) H_-(t_2) H_-(t_3) \mathcal{P}\right. \\ & \left. - \frac{1}{2!} \mathcal{P} T H_-(t) H_-(t_1) H_-(t_2) T H_-(t_3) \mathcal{P}\right). \end{aligned} \quad (22)$$

Inserting now the Hamiltonian H' general definition Equation (5), we obtain immediately using Equation (4):

$$\begin{aligned} \mathcal{K}_4(t) = & -\frac{1}{\hbar^4 2!} \sum_{mkoq} A_m A_k A_o A_q \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \int_{t_0}^t dt_3 \\ & \cdot \langle 2(TF_+^m(t) F_-^k(t_1)) \langle TF_+^o(t_2) F_-^q(t_3) \rangle \\ & \times [[TS_-^m(t) S_+^k(t_1) S_-^o(t_2) S_+^q(t_3)] \\ & - [TS_-^m(t) S_+^k(t_1)][TS_-^o(t_2) S_+^q(t_3)]] \\ & + 2\langle TF_+^m(t) F_+^k(t_1) \rangle \langle TF_+^o(t_2) F_-^q(t_3) \rangle \\ & \times [[TS_-^m(t) S_-^k(t_1) S_-^o(t_2) S_+^q(t_3)] \\ & - [TS_-^m(t) S_-^k(t_1)][TS_-^o(t_2) S_+^q(t_3)]] \\ & + \langle TF_+^m(t) F_-^k(t_1) \rangle \langle TF_+^o(t_2) F_+^q(t_3) \rangle \\ & \times [[TS_-^m(t) S_+^k(t_1) S_-^o(t_2) S_-^q(t_3)] \\ & - [TS_-^m(t) S_+^k(t_1)][TS_-^o(t_2) S_-^q(t_3)]] \\ & + \langle TF_+^m(t) F_+^k(t_1) \rangle \langle TF_+^o(t_2) F_+^q(t_3) \rangle \\ & \times [[TS_-^m(t) S_-^k(t_1) S_-^o(t_2) S_-^q(t_3)] \\ & - [TS_-^m(t) S_-^k(t_1)][TS_-^o(t_2) S_-^q(t_3)]]]. \end{aligned} \quad (23)$$

The time-ordering operator acts only on superoperators within each bracket. Products of two bath

correlation functions appear here. As in \mathcal{K}_2 , the system part is still an operator in the system space. Due to the trace conservation rule the system part always starts with a system-operator of time t , which must be larger than all other times in these terms, since this part is generated by the left-most operator H' in Equation (8). Note the appearance of system operators in different partial time orderings. This did not arise in second order, where the partial time ordering leads to only one possible combination of system operators in second order.

In fourth order, all non-vanishing contributions of $+/-$ operators appear. The products of two pairs of time-ordered operators compensate the contribution from the second order, which will appear in the following ways, since the TCL, also in second order, includes some perturbative contributions, so if we integrate Equation (14):

$$\mathcal{P}\rho(t)|_2 = \int_{t_0}^t dt' \mathcal{K}_2(t') \mathcal{P}\rho(t') \quad (24)$$

and reinsert this equation into itself, we get:

$$\mathcal{P}\rho(t)|_2 = \int_{t_0}^t \int_{t_0}^{t'} dt'' dt' \mathcal{K}_2(t') \mathcal{K}_2(t'') \mathcal{P}\rho(t''). \quad (25)$$

These second-order contributions will be canceled by the terms of \mathcal{K}_4 , which contain two pairs of time-ordered operators. The term including one time-ordered operator and four time-ordered operators contains the correct fourth-order contribution.

\mathcal{K}_4 can be evaluated in the Markovian approximation, therefore the time-ordering operators have to be applied; analog to second order the integration times in Equation (23) have to be transformed to time differences and after that the upper integration bound is set to infinity.

Markovian approximation is usually applied to the weak coupling, even in this limit the fourth-order Markovian contribution can be important. It can be important if small corrections to the second-order result are needed or if the second order contribution is forbidden by energy conservation. One example is the phonon-assisted relaxation of electrons and holes from wetting layer to quantum dots, here one-phonon processes (second-order contribution) are forbidden by energy conservation and two-phonon processes are allowed (fourth-order contribution) [23].

6. Higher order cumulants

We now recast the higher order contribution of the relaxation equations in terms of the bath correlation functions and the system operators both formulated in

$+/-$ representation. To that end we insert Equation (5) into Equation (29) and apply again Wick's theorem in the $+/-$ representation. We obtain:

$$\begin{aligned} \mathcal{K}_{2n}(t) &= \frac{(-1)^n}{\hbar^{2n}} 2^{1-n} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{2n-1}} dt_{2n-1} \\ &\times \sum_{\sigma_1 \sigma_2 \dots \sigma_{2n}} A_{\sigma_1} A_{\sigma_2} \dots A_{\sigma_{2n}} \\ &\times \sum_{s_1, \dots, s_n = +1, -1} \prod_{i=1}^n 2^{\frac{s_i+1}{2}} \left\langle TF_+^{\sigma_1}(t) F_{-s_1}^{\sigma_2}(t_1) \right\rangle \\ &\times \prod_{\mu_1=1}^{n-1} \left\langle TF_+^{\sigma_{2\mu_1+1}}(t_{2\mu_1}) F_{-s_{1+\mu_1}}^{\sigma_{2\mu_1+2}}(t_{2\mu_1+1}) \right\rangle \\ &\times \sum_{q=1}^{n-1} (-1)^q \sum_{\substack{v_1+v_2+\dots+v_q=n-1 \\ v_1 \geq 0, v_j > 0}} \left(TS_-^{\sigma_1}(t) S_{s_1}^{\sigma_2}(t_1) \right. \\ &\times \prod_{\mu_1=1}^{v_1} S_-^{\sigma_{2\mu_1+1}}(t_{2\mu_1}) S_{s_{\mu_1+1}}^{\sigma_{2\mu_1+2}}(t_{2\mu_1+1}) \Big) \\ &\times \left(T \prod_{\mu_2=1}^{v_2} S_-^{\sigma_{2v_1+2\mu_2+1}}(t_{2v_1+2\mu_2}) S_{s_{v_1+\mu_2+1}}^{\sigma_{2v_1+2\mu_2+2}}(t_{2\mu_2+2v_1+1}) \right) \\ &\dots \\ &\times \left(T \prod_{\mu_q=1}^{v_q} S_-^{\sigma_{2\sum_{i=1}^{q-1} v_i+2\mu_q+1}} \left(t_{2\sum_{i=1}^{q-1} v_i+2\mu_q} \right) \right. \\ &\times S_{s_{\sum_{i=1}^{q-1} v_i+\mu_q+1}}^{\sigma_{2\sum_{i=1}^{q-1} v_i+2\mu_q+2}} \left(t_{2\mu_q+2\sum_{i=1}^{q-1} v_i+1} \right) \Big). \end{aligned}$$

All possible combinations of bath correlations function with $++$, $+/-$ now appear. These are directly connected to $-$, $-+$ system operators S , so that the trace is preserved in this equation. The system operators appear in any possible partial time ordering, so that all possible processes in $2n$ order H' are contained, where again the terms with several time ordering operators account to remove the $2n$ contribution from smaller orders, as in the fourth order case.

7. Conclusions

In this paper we derived closed expressions for the relaxation equations of a system coupled to a harmonic bath in all orders of the system bath coupling. These expressions are formulated using the $+/-$ super-operator representation. These results can be useful for the simulation of dephasing, transport and relaxation in optical experiments.

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Appendix

Van Kampen's prescription for higher order cumulants

Van Kampen had formulated in [8] a general rule for the n th order cumulant $\mathcal{K}_n(t)$. Following the notation of [9],

we have:

$$\begin{aligned} \mathcal{K}_n(t) &= \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \\ &\times \int_{t_0}^{t_{n-2}} dt_{n-1} \langle H'_-(t) H'_-(t_1) H'_-(t_2) \cdots H'_-(t_{n-1}) \rangle_{oc}. \end{aligned} \quad (26)$$

Here the ordered cumulant $\langle \dots \rangle_{oc}$ is defined as:

$$\begin{aligned} &\langle H'_-(t) H'_-(t_1) H'_-(t_2) \cdots H'_-(t_{n-1}) \rangle_{oc} \\ &= \sum_q (-1)^q \mathcal{P} H'_-(t) \cdots H'_-(t_i) \mathcal{P} H'_-(t_j) \cdots \\ &\times H'_-(t_k) \mathcal{P} H'_-(t_l) \cdots H'_-(t_m) \mathcal{P} \cdots \mathcal{P}. \end{aligned} \quad (27)$$

Here every summand, that obeys the following rules, should be included in the sum:

- Write down a string of the form $\mathcal{P} H'_- \dots H'_- \mathcal{P}$ with n factors of H'_- .
- Add an arbitrary number q of factors \mathcal{P} , $q=0, 1, \dots$. Since $\mathcal{P}^2 = \text{Id}$, in between two \mathcal{P} must be at least one H'_- .
- Add time arguments to the H'_- operators in any permutation of t_1, t_2, \dots, t_n except that the time arguments in between two operators \mathcal{P} have to be time ordered and the first argument is always t .

With the help of these rules and the time ordering operators, Equation (26) can be formalized as:

$$\begin{aligned} \mathcal{K}_n(t) &= \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-2}} dt_{n-1} \sum_{q=0}^{n-1} (-1)^q \sum_{\substack{v_1+v_2+\dots+v_q=n-1 \\ v_i \geq 0, v_i > 0}} \frac{1}{v_1! \cdots v_q!} \\ &\times \mathcal{P} \left[T H'_-(t) \prod_{\mu_1=1}^{v_1} H'_-(t_{\mu_1}) \right] \mathcal{P} \left[T \prod_{\mu_2=1}^{v_2} H'_-(t_{v_1+\mu_2}) \right] \mathcal{P} \cdots \\ &\times \mathcal{P} \left[T \prod_{\mu_q=1}^{v_q} H'_-(t_{\sum_{j=1}^{q-1} v_j + \mu_q}) \right] \mathcal{P}. \end{aligned} \quad (28)$$

Since the odd moments vanish for our model, the odd cumulant vanishes as well. The even cumulants in the $+$ -representation finally take the form:

$$\begin{aligned} \mathcal{K}_{2n}(t) &= \left(\frac{-1}{\hbar^2}\right)^n \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{2n-1}} dt_{2n-1} \sum_{q=0}^{n-1} (-1)^q \\ &\times \sum_{\substack{v_1+v_2+\dots+v_q=n-1 \\ \dots+v_q=n-1 \\ v_i \geq 0, v_i > 0}} \frac{1}{(2v_1+1)!(2v_2)! \cdots (2v_q)!} \\ &\times \mathcal{P} \left[T H'_-(t) H'_-(t_1) \prod_{\mu_1=1}^{2v_1} H'_-(t_{\mu_1+1}) \right] \\ &\times \mathcal{P} \left[T \prod_{\mu_2=1}^{2v_2} H'_-(t_{1+2v_1+\mu_2}) \right] \mathcal{P} \cdots \\ &\times \mathcal{P} \left[T \prod_{\mu_q=1}^{2v_q} H'_-(t_{1+\sum_{j=1}^{q-1} 2v_j + \mu_q}) \right] \mathcal{P}. \end{aligned} \quad (29)$$