Module V, Lecture 01: Generalized Cumulant Expansion

Generalized cumulant expansion (GCE) method is a generalization and rectification of Redfield theory – it explicitly considers terms of all orders in the perturbation expansion and avoids the convoluted hand-waving (coarse-graining of time, fast correlation function decay, lack of correlation between the system and the bath, *etc.*) that is present in Redfield theory. The core argument of GCE method is that, to be correct, the ensemble averaging must be performed on the exponential propagator applied to the initial state of the system, rather than the differential equation of motion:

$$\hat{\rho}(t)=\exp_{(\mathrm{O})}\left(-i\int_0^t \hat{\hat{H}}(t')\,dt'\right)\hat{\rho}(0) \quad \Rightarrow \quad \left\langle\hat{\rho}(t)\right\rangle=\left\langle\exp_{(\mathrm{O})}\left(-i\int_0^t \hat{\hat{H}}(t')\,dt'\right)\right\rangle\hat{\rho}(0) \tag{1}$$

where angular brackets denote ensemble averaging, $\exp_{(\mathrm{O})}$ denotes a time-ordered exponential (which was discussed in detail in Module I) and the initial state is assumed to be the same for all members of the ensemble. Because the treatment is performed on the general *solution* to the Liouville – von Neumann equation, it has the advantage of being free, at least in the initial formulation, of any assumptions about the statistical properties of the physical system.

If the noise in the system is stationary, we would expect the time propagation superoperator in Equation (1) to also be stationary. The objective of the GCE method is to find the generator $\hat{\hat{L}}$ of the corresponding semigroup:

$$\exp\left(-i\hat{\hat{L}}t\right)=\left\langle\exp_{(\mathrm{O})}\left(-i\int_0^t \hat{\hat{H}}(t')\,dt'\right)\right\rangle \tag{2}$$

Moments and cumulants: random variable case

Let $p(x)$ be the probability distribution of a stochastic variable x. The *n-th moment* of this probability distribution is defined as the expectation value of x^n:

$$\left\langle x^n\right\rangle=\int_{-\infty}^{\infty} x^n p(x)\,dx \tag{3}$$

and the *moment-generating function* as the expectation value of e^{kx}:

$$\left\langle e^{kx}\right\rangle=\int_{-\infty}^{\infty} p(x)e^{kx}\,dx \tag{4}$$

The following relations hold for the power series and derivatives:

$$\left\langle e^{kx}\right\rangle=\sum_{n=0}^{\infty}\frac{k^n}{n!}\int_{-\infty}^{\infty}p(x)x^n dx=\sum_{n=0}^{\infty}\frac{\left\langle x^n\right\rangle}{n!}k^n \quad \Rightarrow \quad \left\langle x^n\right\rangle=\left[\frac{d^n}{dk^n}\left\langle e^{kx}\right\rangle\right]_{k=0} \tag{5}$$

The logarithm of the characteristic function is called the *cumulant-generating function* and its series coefficients $\left\langle\left\langle x^n\right\rangle\right\rangle$ are called *cumulants* of the stochastic variable x:

$$\ln\left\langle e^{kx}\right\rangle=\sum_{n=0}^{\infty}\frac{\left\langle\left\langle x^n\right\rangle\right\rangle}{n!}k^n \quad \Rightarrow \quad \left\langle\left\langle x^n\right\rangle\right\rangle=\left[\frac{d^n}{dk^n}\ln\left\langle e^{kx}\right\rangle\right]_{k=0} \tag{6}$$

Expressions for cumulants in terms of moments may be obtained directly from the definition and Equation (5), for example:

$$\begin{aligned}
\langle\langle x\rangle\rangle &= \left[\frac{d}{dk}\ln\langle e^{kx}\rangle\right]_{k=0} = \left[\frac{1}{\langle e^{kx}\rangle}\frac{d}{dk}\langle e^{kx}\rangle\right]_{k=0} = \left[\frac{d}{dk}\langle e^{kx}\rangle\right]_{k=0} = \langle x\rangle \\
\langle\langle x^2\rangle\rangle &= \left[\frac{d^2}{dk^2}\ln\langle e^{kx}\rangle\right]_{k=0} = \ldots = \langle x^2\rangle - \langle x\rangle^2 \\
\langle\langle x^3\rangle\rangle &= \left[\frac{d^3}{dk^3}\ln\langle e^{kx}\rangle\right]_{k=0} = \ldots = \langle x^3\rangle - 3\langle x^2\rangle\langle x\rangle + 2\langle x\rangle^3 \\
\langle\langle x^4\rangle\rangle &= \left[\frac{d^4}{dk^4}\ln\langle e^{kx}\rangle\right]_{k=0} = \ldots = \langle x^4\rangle - 4\langle x^3\rangle\langle x\rangle - 3\langle x^2\rangle\langle x^2\rangle + 12\langle x^2\rangle\langle x\rangle^2 - 6\langle x\rangle^4
\end{aligned} \tag{7}$$

et cetera. It should be noted that $\langle e^{kx}\rangle = 1$ for $k=0$. The relationship between moments and cumulants may be summarized as follows:

$$\langle e^x\rangle = \sum_{n=0}^{\infty}\frac{\langle x^n\rangle}{n!} = \exp\left[\sum_{n=0}^{\infty}\frac{\langle\langle x^n\rangle\rangle}{n!}\right] \tag{8}$$

Moments and cumulants: random vector case

For an n-element vector of stochastic variables $\{x_1, x_2, \ldots\}$ with the joint probability distribution $p(x_1, x_2, \ldots)$ the moment-generating function is the expectation value of the exponential of an arbitrary linear combination of its elements:

$$\langle e^{k_1x_1+k_2x_2+\ldots}\rangle = \int p(x_1, x_2, \ldots)\, e^{k_1x_1+k_2x_2+\ldots}dV \tag{9}$$

where k_i are the coefficients and the integral is taken over the volume of the space containing $\{x_1, x_2, \ldots\}$. *Joint moments* are defined *via* the derivatives of this function:

$$\langle x_1^{\alpha_1}x_2^{\alpha_2}\ldots\rangle = \left[\frac{\partial^{\alpha_1+\alpha_2+\ldots}}{\partial k_1^{\alpha_1}\partial k_2^{\alpha_2}\ldots}\langle e^{k_1x_1+k_2x_2+\ldots}\rangle\right]_{k_i=0} \tag{10}$$

and *joint cumulants via* power series coefficients of its logarithm:

$$\langle\langle x_1^{\alpha_1}x_2^{\alpha_2}\ldots\rangle\rangle = \left[\frac{\partial^{\alpha_1+\alpha_2+\ldots}}{\partial k_1^{\alpha_1}\partial k_2^{\alpha_2}\ldots}\ln\langle e^{k_1x_1+k_2x_2+\ldots}\rangle\right]_{k_i=0} \tag{11}$$

Expressions for joint cumulants in terms of joint moments follow immediately from Equation (11):

$$\begin{aligned}
\langle\langle x_1\rangle\rangle &= \left[\frac{d}{dk_1}\ln\langle e^{k_1x_1}\rangle\right]_{k_i=0} = \ldots = \langle x_1\rangle \\
\langle\langle x_1x_2\rangle\rangle &= \left[\frac{d^2}{dk_1dk_2}\ln\langle e^{k_1x_1+k_2x_2}\rangle\right]_{k_i=0} = \ldots = \langle x_1x_2\rangle - \langle x_1\rangle\langle x_2\rangle \\
\langle\langle x_1x_2x_3\rangle\rangle &= \left[\frac{d^3}{dk_1dk_2dk_3}\ln\langle e^{k_1x_1+k_2x_2+k_3x_3}\rangle\right]_{k_i=0} = \ldots = \\
&= \langle x_1x_2x_3\rangle - \langle x_1\rangle\langle x_2x_3\rangle - \langle x_2\rangle\langle x_3x_1\rangle - \langle x_3\rangle\langle x_1x_2\rangle + 2\langle x_1\rangle\langle x_2\rangle\langle x_3\rangle
\end{aligned} \tag{12}$$

More work is required to obtain subsequent expansions, but the procedure is largely technical and may easily be coded up in *Mathematica*. Note that Equations (12) simplify for centered stochastic processes.

Kubo's theorem

A general expression for the Taylor series around the origin in the multi-dimensional case is:

$$f\left(x_1,...,x_N\right)=\sum_{\alpha_1=0}^{\infty}...\sum_{\alpha_N=0}^{\infty}\frac{1}{\alpha_1!...\alpha_N!}\left[\frac{\partial^{\alpha_1+...+\alpha_N}f}{\partial x_1^{\alpha_1}...\partial x_N^{\alpha_N}}\right]_{x_i=0}x_1^{\alpha_1}...x_N^{\alpha_N} \tag{13}$$

In combination with Equation (11) this allows us to obtain a series for the cumulant-generating function in terms of cumulants:

$$\ln\left\langle \exp\left(k_1x_1+...+k_Nx_N\right)\right\rangle=\sum_{\alpha_1=0}^{\infty}...\sum_{\alpha_N=0}^{\infty}\frac{\left\langle\left\langle x_1^{\alpha_1}...x_N^{\alpha_N}\right\rangle\right\rangle}{\alpha_1!...\alpha_N!}k_1^{\alpha_1}...k_N^{\alpha_N} \tag{14}$$

where we have implicitly defined $\left\langle\left\langle 1\right\rangle\right\rangle=0$. We will now take advantage of the definition of the Riemann integral:

$$\int_a^b x(t)\,dt=\lim_{\max(\delta t)\to 0}\left(\sum_{i=1}^{N}x(t_i)\,\delta t_i\right) \tag{15}$$

to take the limit of Equation (14) by replacing k_ix_i with $x(t_i)\,\delta t_i$ and noting that terms of higher than first order in any of the δt_i do not survive the limit operation:

$$\ln\left\langle\exp\left(\int_a^b x(t)\,dt\right)\right\rangle=\sum_{n=1}^{\infty}\frac{1}{n!}\int_a^b dt_1\int_a^b dt_2\ldots\int_a^b dt_n\left\langle\left\langle x(t_1)\,x(t_2)\ldots x(t_n)\right\rangle\right\rangle \tag{16}$$

The final expression (published by Ryogo Kubo in 1962) is:

$$\begin{aligned}\left\langle\exp\left(\int_a^b x(t)\,dt\right)\right\rangle&=\exp\left(\sum_{n=1}^{\infty}\frac{1}{n!}\int_a^b dt_1\int_a^b dt_2\ldots\int_a^b dt_n\left\langle\left\langle x(t_1)\,x(t_2)\ldots x(t_n)\right\rangle\right\rangle\right)\\ \left\langle\exp\left(\int_a^b x(t)\,dt\right)\right\rangle&=\exp\left(\sum_{n=1}^{\infty}\int_a^b dt_1\int_a^{t_1} dt_2\ldots\int_a^{t_{n-1}} dt_n\left\langle\left\langle x(t_1)\,x(t_2)\ldots x(t_n)\right\rangle\right\rangle\right)\end{aligned} \tag{17}$$

In this case, no time ordering is necessary because all scalars commute. The second variant of Equation (17) does not require time-ordering.

Generalized cumulant expansion

To relate Kubo's theorem to relaxation theory, we would note that the interaction representation of the Liouville – von Neumann equation

$$\frac{\partial\hat{\sigma}(t)}{\partial t}=-i\hat{\hat{H}}_1^{\mathrm{R}}(t)\,\hat{\sigma}(t) \tag{18}$$

may be formally integrated to yield

$$\hat{\sigma}(t)=\hat{\sigma}(0)+(-i)\int_0^t\hat{\hat{H}}_1^{\mathrm{R}}(t')\,\hat{\sigma}(t')\,dt' \tag{19}$$

this process may be repeated multiple times, with the eventual result that

$$\hat{\sigma}(t)=\hat{\sigma}(0)+\sum_{n=1}^{\infty}(-i)^n\int_0^t dt_1\int_0^{t_1}dt_2\ldots\int_0^{t_{n-1}}dt_n\hat{\hat{H}}_1^{\mathrm{R}}(t_1)\,\hat{\hat{H}}_1^{\mathrm{R}}(t_2)\ldots\hat{\hat{H}}_1^{\mathrm{R}}(t_n)\,\hat{\sigma}(0) \tag{20}$$

As described in Lecture 8, this defines the *time-ordered exponential* propagator that takes the system forward from 0 to t in the case where the Hamiltonian superoperator is time-dependent:

$$\hat{\sigma}(t)=\exp_{(\mathrm{O})}\left(-i\int_0^t \hat{\hat{H}}_1^{\mathrm{R}}(t')\,dt'\right)\hat{\sigma}(0) \tag{21}$$

Time ordering is now necessary because $\hat{\hat{H}}_1^{\mathrm{R}}(t)$ need not commute with itself at different times. This brings us back to Equation (2), for which we can now take the ensemble average and express it in terms of cumulants using Equation (17):

$$\left\langle \exp_{(\mathrm{O})}\left(-i\int_0^t \hat{\hat{H}}^{\mathrm{R}}(t')\,dt'\right)\right\rangle=\exp\left(\sum_{n=1}^{\infty}(-i)^n\int_0^t dt_1\int_0^{t_1}dt_2\ldots\int_0^{t_{n-1}}dt_n\left\langle\left\langle \hat{\hat{H}}^{\mathrm{R}}(t_1)\hat{\hat{H}}^{\mathrm{R}}(t_2)\ldots\hat{\hat{H}}^{\mathrm{R}}(t_n)\right\rangle\right\rangle\right) \tag{22}$$

The first few terms in the expansion on the right hand side are (assuming that $\hat{\hat{H}}_1^{\mathrm{R}}(t)$ is a centered stochastic process to make the first moments vanish):

$$\begin{aligned}
&\hat{\hat{K}}_1=0\\
&\hat{\hat{K}}_2=(-i)^2\int_0^t dt_1\int_0^{t_1}dt_2\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_1)\hat{\hat{H}}_1^{\mathrm{R}}(t_2)\right\rangle\\
&\hat{\hat{K}}_3=(-i)^3\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_1)\hat{\hat{H}}_1^{\mathrm{R}}(t_2)\hat{\hat{H}}_1^{\mathrm{R}}(t_3)\right\rangle\\
&\hat{\hat{K}}_4=(-i)^4\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4\left(A+B+C+D\right)\\
&\quad A=\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_1)\hat{\hat{H}}_1^{\mathrm{R}}(t_2)\hat{\hat{H}}_1^{\mathrm{R}}(t_3)\hat{\hat{H}}_1^{\mathrm{R}}(t_4)\right\rangle\\
&\quad B=-\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_1)\hat{\hat{H}}_1^{\mathrm{R}}(t_2)\right\rangle\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_3)\hat{\hat{H}}_1^{\mathrm{R}}(t_4)\right\rangle\\
&\quad C=-\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_1)\hat{\hat{H}}_1^{\mathrm{R}}(t_3)\right\rangle\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_2)\hat{\hat{H}}_1^{\mathrm{R}}(t_4)\right\rangle\\
&\quad D=-\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_1)\hat{\hat{H}}_1^{\mathrm{R}}(t_4)\right\rangle\left\langle \hat{\hat{H}}_1^{\mathrm{R}}(t_2)\hat{\hat{H}}_1^{\mathrm{R}}(t_3)\right\rangle
\end{aligned} \tag{23}$$

The simple connection from the generalized cumulant expansion truncated at the second term to Redfield theory is left as an exercise.