University of Washington
Department of Chemistry
Chemistry 553
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Lecture 25: The Stochastic Liouville Equation

05/23/11

Text Reading: Ch 21,22

A. Introduction

- In the last lecture we treated the Kubo oscillator, a periodic motion which is also affected by a stochastic process. Here a dynamical variable has an equation of motion:

$$\frac{dA}{dt} = i\omega(t)A \text{ where } \omega(t) = \omega_0 + \delta\omega(t) \tag{25.1}$$

- Solution of (25.1) leads us to the correlation function expression:

$$\begin{aligned} C(t) &= \left\langle A(t)A^*(0)\right\rangle = \left|A(0)\right|^2 \left\langle \exp\left\{ i\int_0^t \omega(s)\,ds \right\}\right\rangle \\ &= \left|A(0)\right|^2 e^{i\omega_0 t}\left\langle \exp\left\{ i\int_0^t \delta\omega(s)\,ds \right\}\right\rangle = \left|A(0)\right|^2 e^{i\omega_0 t}\phi(t) \end{aligned} \tag{25.2}$$

- Note the correlation function must obey (25.1) in the sense that

$$\frac{dC(t)}{dt} = i\omega(t)C(t) \tag{25.3}$$

- This problem can be expressed in terms of the the Stochastic Liouville Equation (SLE). Kubo introduced the SLE to treat a general class of problems where the Liouvillian is modulated as a result of a random process.
- There is a classical SLE and a quantum mechanical form. We will deal with the latter. Recall the quantum mechanical Liouville equation

$$\frac{\partial\rho}{\partial t} = -\frac{i}{\hbar}\left[H,\rho\right] = -\frac{i}{\hbar}\left[H_0 + H_1(t),\rho\right] = -\left(L_0 + L_1\right)\rho \tag{25.4}$$

where L_1 is assumed to arise from a stochastic process.

- Equation (25.4) is sometimes written in the form:

$$\frac{\partial\rho}{\partial t} = -\left(i\tilde{\omega}_0 + \tilde{\pi}\right)\rho \tag{25.5}$$

where $\tilde{\omega}_0$ represents the natural frequencies of the unperturbed system (eigenvalues of H_0) and $\tilde{\pi}$ is called the relaxation operator and arises from the stochastic process.

- It is also the case that C(t) obeys the equation:

$$\frac{\partial C(t)}{\partial t} = \left(i\tilde{\omega}_0 + \tilde{\pi}\right) C(t) \tag{25.6}$$

(25.7)

B. Formal Solution of the SLE

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- We can easily integrate 25.6:

$$C(t) = e^{(i\omega_0 + \pi)t} C(0) \tag{25.8}$$

- The absorption line shape I(w) is given by:

$$I(\omega) = \mathrm{Re}\int_{-\infty}^{+\infty} e^{-i\omega t} C(t)\, dt = \mathrm{Re}\int_{-\infty}^{+\infty} e^{-i\omega t} e^{(i\omega_0 + \pi)t} C(0)\, dt = \mathrm{Re}\int_{-\infty}^{+\infty} e^{-it(\omega - \omega_0)} e^{\pi t} C(0) dt$$

- $= 2\int_0^{+\infty} \cos\left[(\omega - \omega_0)t\right] e^{\pi t} C(0) dt = -2\dfrac{\pi}{(\omega - \omega_0)^2 + \pi^2} C(0)$

$$= -2\,\mathrm{Re}\left\{\frac{i(\omega - \omega_0) + \pi}{\left(i(\omega - \omega_0) + \pi\right)\left(-i(\omega - \omega_0) + \pi\right)} C(0)\right\} = -2\,\mathrm{Re}\left\{\left(-i(\omega - \omega_0) + \pi\right)^{-1} C(0)\right\}$$

(25.9)

C. Example: Two Site Jump

- To connect with the earlier theory, suppose we discretize the stochastic process such that the system passes through a large number N of states

$$C(t) = |A(0)|^2 \left\langle \exp\left\{i\int_0^t \omega(s)\, ds\right\}\right\rangle \approx |A(0)|^2 \left\langle \exp\left\{i\sum_{i=1}^{N} \omega_i \Delta t_i\right\}\right\rangle \tag{25.10}$$

where we assume $\Delta t_i = \Delta t = t / N$. Then there are a finite number of states N and (25.6) may be put in eth vector/matrix form:

$$\frac{\partial C_\beta(t)}{\partial t} = i\tilde{\omega}_\beta C_\beta(t) + \sum_\alpha \tilde{\pi}_{\beta\alpha} C_\alpha(t)$$

- In this notation $C_\beta(t)$ is the decorrelation of the system which exists at ω_β, i.e.

$$C_\beta(t) = |A(0)|^2 \left\langle \exp\left\{i\int_0^t \omega(s)\, ds\right\}\right\rangle = |A(0)|^2 e^{i\omega_{\beta t}} \left\langle \exp\left\{i\int_0^t \delta\omega(s)\, ds\right\}\right\rangle \tag{25.11}$$

- In this example a system (e.g. a nuclear spin) jumps randomly between two sites. In site 1 the frequency is δ and in site two the frequency is –δ. Therefore $\omega_0 = \pm\delta$ or in a matrix representation

$$\omega_0 = \begin{pmatrix} \delta & 0 \\ 0 & -\delta \end{pmatrix} \tag{25.12}$$

- The matrix Γ describes the jump rates between the sites. The matrix representation for Γ is

$$\pi = \kappa\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \tag{25.13}$$

- From (25.11) the lineshape is

$$I(\omega) = -2\,\mathrm{Re}\left\{\vec{1}\bullet\left(-i\left(\omega-\tilde{\omega}_0\right)+\tilde{\pi}\right)^{-1}\bullet\vec{C}(0)\right\} = -2\,\mathrm{Re}\left\{\vec{1}\bullet\left(i\left(\omega-\tilde{\omega}_0\right)+\tilde{\pi}\right)^{-1}\bullet\vec{W}(0)\right\}$$

$$= -2\,\mathrm{Re}\left\{\begin{pmatrix}1 & 1\end{pmatrix}\bullet\begin{pmatrix} i(-\omega+\delta)-\kappa & \kappa \\ \kappa & -i(\omega+\delta)-\kappa \end{pmatrix}^{-1}\bullet\begin{pmatrix}\frac{1}{2}\\ \frac{1}{2}\end{pmatrix}\right\} = -2\,\mathrm{Re}\left\{\begin{pmatrix}1 & 1\end{pmatrix}\bullet A^{-1}\bullet\begin{pmatrix}\frac{1}{2}\\ \frac{1}{2}\end{pmatrix}\right\} \quad (25.14)$$

- In (25.14) the initial condition vector C(0)=W(0) assumes both sites are equally populated initially. To obtain the lineshape we need the matrix inverse $\left(-i\left(\omega-\omega_0\right)+\pi\right)^{-1}$. Upon inverting A we find

$$I(\omega) = -2\,\mathrm{Re}\left\{\begin{pmatrix}1 & 1\end{pmatrix}\bullet A^{-1}\bullet\begin{pmatrix}\frac{1}{2}\\ \frac{1}{2}\end{pmatrix}\right\} = \frac{4\kappa^2\omega}{\left(\delta^2-\omega^2\right)^2+4\kappa^2\omega^2} \qquad (25.15)$$

  - Below the spectroscopic line shape according to equation (23.12) is plotted for δ=200 Hz. for k= 10, 20, 100, 400, and 1000 Hz.