

## Module VI, Lecture 02: Stochastic Liouville Equation

### General formalism

For each specific molecule in the ensemble, the Liouville – von Neumann equation is a stochastic differential equation defining the stochastic process  $\hat{\rho}(t)$ :

$$\frac{\partial}{\partial t} \hat{\rho}(t) = -i\hat{H}\hat{\rho}(t) = -i\left[\hat{H}_0 + \hat{H}_1(\vec{x})\right]\hat{\rho}(t) \quad (1)$$

where  $\hat{H}_0$  is the intrinsic part of the Hamiltonian commutation superoperator and  $\hat{H}_1$  is the part that depends on some external parameters  $\vec{x}$ , such as coordinates, angles, etc.

We will now perform a change of perspective – instead of considering the dynamics of the density matrix  $\hat{\rho}(t)$  as a function of time, we will consider the dynamics of probability  $P(\hat{\rho}, t)$  of the system having density matrix  $\hat{\rho}$  at time  $t$ . This would place the density matrix on the same conceptual level as spatial coordinates – we can now similarly define the time-dependent probability  $P(\vec{x}, \hat{\rho}, t)$  of system being in a spatial point  $\vec{x}$  in the spin state  $\hat{\rho}$ . Because the spatial probability distribution is effectively “concentration”, it is reasonable to assume that, in the absence of spin dynamics, the spatial probability density of molecules in a particular spin state  $\hat{\rho}$  evolves according to some simple deterministic law:

$$\left. \frac{\partial P(\vec{x}, \hat{\rho}, t)}{\partial t} \right|_{\hat{\rho}} = \hat{D}P(\vec{x}, \hat{\rho}, t) \quad (2)$$

where  $\hat{D}$  is the spatial diffusion operator that depends on the physical nature of the diffusion process. The derivative of the probability  $P(\vec{x}, \hat{\rho}, t)$  with respect to the spin coordinates is less obvious. We will first note that, in the absence of spatial dynamics, the spin evolution is governed completely by the Liouville – von Neumann equation, and therefore:

$$P(\vec{x}, \hat{\rho}, t + \Delta t) \Big|_{\vec{x}} = P(\vec{x}, e^{-i\hat{H}\Delta t} \hat{\rho}, t) \Big|_{\vec{x}} \quad (3)$$

Taking a Taylor expansion of this expression with respect to the time increment then yields:

$$\begin{aligned} P(\vec{x}, e^{-i\hat{H}\Delta t} \hat{\rho}, t) &= P(\vec{x}, \hat{\rho}, t) + \left\langle \nabla_{\hat{\rho}} P(\vec{x}, \hat{\rho}, t) \Big| e^{-i\hat{H}\Delta t} \hat{\rho} - \hat{\rho} \right\rangle + O\left(\left\| e^{-i\hat{H}\Delta t} \hat{\rho} - \hat{\rho} \right\|^2\right) = \\ &= P(\vec{x}, \hat{\rho}, t) + \left\langle \nabla_{\hat{\rho}} P(\vec{x}, \hat{\rho}, t) \Big| -i\hat{H}\hat{\rho} \right\rangle \Delta t + O(\Delta t^2) \end{aligned} \quad (4)$$

With this in place, for an infinitesimal displacement forward in time with frozen space coordinates:

$$\begin{aligned} \left. \frac{\partial P(\vec{x}, \hat{\rho}, t)}{\partial t} \right|_{\vec{x}} &= \lim_{\Delta t \rightarrow 0} \frac{P(\vec{x}, \hat{\rho}, t + \Delta t) - P(\vec{x}, \hat{\rho}, t)}{\Delta t} = \left\langle \nabla_{\hat{\rho}} P(\vec{x}, \hat{\rho}, t) \Big| -i\hat{H}\hat{\rho} \right\rangle = \\ &= \left\langle \nabla_{\hat{\rho}} \Big| P(\vec{x}, \hat{\rho}, t) (-i\hat{H}\hat{\rho}) \right\rangle - P(\vec{x}, \hat{\rho}, t) \left\langle \nabla_{\hat{\rho}} \Big| -i\hat{H}\hat{\rho} \right\rangle \end{aligned} \quad (5)$$

The second term in this expression is zero because the spin Hamiltonian is traceless:

$$\left\langle \nabla_{\hat{\rho}} \Big| -i\hat{H}\hat{\rho} \right\rangle = -i \sum_k \frac{\partial}{\partial \rho_k} \left[ \hat{H}\hat{\rho} \right]_k = -i \sum_k \frac{\partial}{\partial \rho_k} \sum_m H_{km} \rho_m = -i \sum_k H_{kk} = 0 \quad (6)$$

And so, after merging Equations (2) and (5), we get the partial differential equation governing the dynamics of our probability distribution:

$$\frac{\partial}{\partial t} P(\bar{x}, \hat{\rho}, t) = \left\langle \nabla_{\hat{\rho}} \left| P(\bar{x}, \hat{\rho}, t) \left( -i\hat{H}\hat{\rho} \right) \right\rangle + \hat{D}P(\bar{x}, \hat{\rho}, t) \quad (7)$$

We can now obtain the equation of motion for the ensemble-averaged density matrix  $\overline{\hat{\rho}(\bar{x}, t)}$ :

$$\overline{\hat{\rho}(\bar{x}, t)} = \int \hat{\rho} P(\bar{x}, \hat{\rho}, t) dV_{\hat{\rho}} \quad (8)$$

by integrating the probability distribution over the volume  $V_{\hat{\rho}}$  of the spin state space. Note that this is a very high-dimensional integral – our only hope is to take it analytically. This can actually be done:

$$\begin{aligned} \frac{\partial}{\partial t} \overline{\hat{\rho}(\bar{x}, t)} &= \int \left( \frac{\partial}{\partial t} P(\bar{x}, \hat{\rho}, t) \right) \hat{\rho} dV_{\hat{\rho}} = \int \left( \left\langle \nabla_{\hat{\rho}} \left| P(\bar{x}, \hat{\rho}, t) \left( -i\hat{H}\hat{\rho} \right) \right\rangle + \hat{D}P(\bar{x}, \hat{\rho}, t) \right) \hat{\rho} dV_{\hat{\rho}} = \\ &= \int \left\langle \nabla_{\hat{\rho}} \left| P(\bar{x}, \hat{\rho}, t) \left( -i\hat{H}\hat{\rho} \right) \right\rangle \hat{\rho} dV_{\hat{\rho}} + \int \hat{D}P(\bar{x}, \hat{\rho}, t) \hat{\rho} dV_{\hat{\rho}} \end{aligned} \quad (9)$$

The second integral is easy:

$$\int \hat{D}P(\bar{x}, \hat{\rho}, t) \hat{\rho} dV_{\hat{\rho}} = \hat{D} \int P(\bar{x}, \hat{\rho}, t) \hat{\rho} dV_{\hat{\rho}} = \hat{D} \overline{\hat{\rho}(\bar{x}, t)} \quad (10)$$

and the first integral can be taken using the multi-dimensional version of integration by parts:

$$\int_V f \langle \nabla | \bar{g} \rangle dV = \oint_S f \langle \bar{g} | d\bar{s} \rangle - \int_V \langle \bar{g} | \nabla f \rangle dV \quad (11)$$

in which the surface integral would be zero because the integration surface can always be chosen to lie outside the unit ball containing the density matrix. Therefore:

$$\begin{aligned} \int \left\langle \nabla_{\hat{\rho}} \left| P(\bar{x}, \hat{\rho}, t) \left( -i\hat{H}\hat{\rho} \right) \right\rangle \hat{\rho} dV_{\hat{\rho}} &= \int P(\bar{x}, \hat{\rho}, t) \left( -i\hat{H}\hat{\rho} \right) dV_{\hat{\rho}} = \\ &= -i\hat{H} \int \hat{\rho} P(\bar{x}, \hat{\rho}, t) dV_{\hat{\rho}} = -i\hat{H} \overline{\hat{\rho}(\bar{x}, t)} \end{aligned} \quad (12)$$

and so we finally get (after dropping the bars):

$$\frac{\partial}{\partial t} \hat{\rho}(\bar{x}, t) = -i\hat{H}(\bar{x}) \hat{\rho}(\bar{x}, t) + \hat{D} \hat{\rho}(\bar{x}, t) \quad (13)$$

where  $\hat{H}$  is the Hamiltonian commutation superoperator and  $\hat{D}$  is the operator from the equation describing the spatial dynamics of the system in those coordinates. Equation (13) is known as the *stochastic Liouville equation* (SLE).

### General solution

Two general styles of solving Equation (13) differ in the treatment of the spatial diffusion problem – it may either be solved on a discrete grid (in which case the diffusion operator becomes a matrix in what is essentially finite difference formalism with a density matrix defined at each grid point) or solved in a continuous representation using a spatial basis set (eigenfunctions of the diffusion operator are generally a good choice). The first option is more general, but the second option has historically appeared first.

Consider an expansion of the Hamiltonian commutation superoperator in terms of a complete orthonormal set of functions  $g_k(\bar{x})$  of space variables and static superoperators  $\hat{Q}_k$ :

$$\hat{H}(\bar{x}) = \sum_n g_n(\bar{x}) \hat{Q}_n, \quad \hat{D}g_k(\bar{x}) = \sum_m D_{mk} g_m(\bar{x}), \quad D_{mk} = \langle g_m | \hat{D} | g_k \rangle \quad (14)$$

The state vector would admit a similar expansion, but with a time-dependent spin part:

$$\hat{\rho}(\bar{x}, t) = \sum_k g_k(\bar{x}) \hat{\rho}_k(t) \quad (15)$$

With this notation in place, Equation (13) can be re-written as:

$$\sum_k g_k(\bar{x}) \frac{\partial \hat{\rho}_k(t)}{\partial t} = -i \sum_{nk} g_n(\bar{x}) g_k(\bar{x}) \hat{Q}_n \hat{\rho}_k(t) + \sum_{nk} D_{nk} g_n(\bar{x}) \hat{\rho}_k(t) \quad (16)$$

Taking the scalar product with each spatial basis function  $g_m(\bar{x})$  in turn yields

$$\left\{ \frac{\partial \hat{\rho}_m(t)}{\partial t} = -i \sum_{nk} c_{nkm} \hat{Q}_n \hat{\rho}_k(t) + \sum_k D_{mk} \hat{\rho}_k(t) = \sum_k \left[ -i \sum_n c_{nkm} \hat{Q}_n + \Gamma_{mk} \hat{E} \right] \hat{\rho}_k(t) \right. \quad (17)$$

where the structure coefficients of the algebra of spatial functions are defined as:

$$c_{nkm} = \int g_n(\bar{x}) g_k(\bar{x}) g_m^*(\bar{x}) dV \quad (18)$$

where  $V$  is the volume of the spatial coordinate space. Finally after collecting a few terms, we get the following system of equations:

$$\left\{ \frac{\partial \hat{\rho}_m(t)}{\partial t} = \sum_k \left[ -i \hat{H}_{km} + D_{mk} \hat{E} \right] \hat{\rho}_k(t), \quad \hat{H}_{km} = \sum_n c_{nkm} \hat{Q}_n \right. \quad (19)$$

It may be solved using standard techniques. The sums are, in principle, infinite, but in practice they can be truncated according to a user-specified accuracy tolerance (as we shall see later, the higher ranks decay faster). Note that the matrix dimensions involved in solving this system are considerably greater than in BRW theory – essentially the spin state space is crossed with the space state space, and the latter can be huge. SLE solutions are therefore only practical for the smallest spin systems.

### SLE treatment of isotropic rotational diffusion

For isotropic rotational diffusion Wigner functions are a natural spatial basis set. Using the spherical tensor expansion for both the Hamiltonian and the density matrix, we get:

$$\begin{aligned} \hat{H}(\Omega) &= \sum_{km} \mathcal{D}_{km}^{(2)}(\Omega) \hat{Q}_{km}, & \hat{D} &= -D(\hat{L}_X^2 + \hat{L}_Y^2 + \hat{L}_Z^2) \\ \hat{\rho}(\Omega, t) &= \sum_{lkm} \mathcal{D}_{km}^{(l)}(\Omega) \hat{r}_{km}^{(l)}(t), & \hat{D} \mathcal{D}_{km}^{(l)}(\Omega) &= -Dl(l+1) \mathcal{D}_{km}^{(l)}(\Omega) \end{aligned} \quad (20)$$

where  $\Omega$  is a parameterization of  $SO(3)$ ,  $\{\hat{L}_X, \hat{L}_Y, \hat{L}_Z\}$  are its generators and  $D$  is the rotational diffusion constant. Note the sum over ranks for  $\hat{\rho}(\Omega, t)$ . With this notation in place, the SLE becomes:

$$\begin{aligned} \sum_{lkm} \mathcal{D}_{km}^{(l)}(\Omega) \frac{\partial}{\partial t} \hat{r}_{km}^{(l)}(t) &= -i \sum_{lkmnpq} \mathcal{D}_{km}^{(2)}(\Omega) \mathcal{D}_{pq}^{(l)}(\Omega) \hat{Q}_{km} \hat{r}_{pq}^{(l)}(t) - D \sum_{lkm} l(l+1) \mathcal{D}_{km}^{(l)}(\Omega) \hat{r}_{km}^{(l)}(t) \\ \mathcal{D}_{km}^{(2)}(\Omega) \mathcal{D}_{pq}^{(l)}(\Omega) &= \sum_{L=|l-2|}^{l+2} \sum_{MN} C_{2,k,l,p}^{L,M} C_{2,m,l,q}^{L,N} \mathcal{D}_{MN}^{(L)}(\Omega) \end{aligned} \quad (21)$$

where  $C_{l,m,l',m'}^{L,M}$  are Clebsch-Gordan coefficients. After separating the ranks and projections of the Wigner functions, we get:

$$\left\{ \frac{\partial}{\partial t} \hat{r}_{MN}^{(L)}(t) = -i \sum_{lkmnpq} C_{2,k,l,p}^{L,M} C_{2,m,l,q}^{L,N} \hat{Q}_{km} \hat{r}_{pq}^{(l)}(t) - DL(L+1) \hat{r}_{MN}^{(L)}(t) \right. \quad (22)$$

If systems start off uniformly distributed over directions and in the same spin state  $\hat{\rho}_0$ , the initial condition becomes:

$$\hat{r}_{0,0}^{(0)}(0) = \hat{\rho}_0 \quad \hat{r}_{km}^{(l)}(0) = 0 \quad (23)$$

Analytical solutions of Equation (22), even for simple systems, tend to be quite cumbersome. Consider a simple example of a single spin with an axial secular Zeeman interaction, tumbling isotropically:

$$\begin{aligned} \hat{H} &= \omega \hat{L}_Z + a \hat{T}_{2,0}(L, B) \mathcal{D}_{0,0}^{(2)}(\Omega), & \hat{D} &= -D(\hat{L}_X^2 + \hat{L}_Y^2 + \hat{L}_Z^2) \\ \hat{\rho}(\Omega, t) &= \sum_{lkm} \mathcal{D}_{km}^{(l)}(\Omega) \hat{r}_{km}^{(l)}(t), & \hat{D} \mathcal{D}_{km}^{(l)}(\Omega) &= -Dl(l+1) \mathcal{D}_{km}^{(l)}(\Omega) \end{aligned} \quad (24)$$

In the rotating frame with respect to the carrier Zeeman interaction term  $\omega \hat{L}_Z$ , the SLE becomes:

$$\sum_{lkm} \mathcal{D}_{km}^{(l)}(\Omega) \frac{\partial}{\partial t} \hat{r}_{km}^{(l)}(t) = -ia \hat{T}_{2,0} \mathcal{D}_{0,0}^{(2)}(\Omega) \sum_{lkm} \mathcal{D}_{km}^{(l)}(\Omega) \hat{r}_{km}^{(l)}(t) - D \sum_{lkm} l(l+1) \mathcal{D}_{km}^{(l)}(\Omega) \hat{r}_{km}^{(l)}(t) \quad (25)$$

The product of Wigner functions splits *via* Clebsch-Gordan relation into several terms:

$$\mathcal{D}_{km}^{(l)}(\Omega) \mathcal{D}_{0,0}^{(2)}(\Omega) = \sum_{L=|l-2|}^{l+2} \sum_{M=-L}^L \sum_{N=-L}^L C_{l,k,2,0}^{L,M} C_{l,m,2,0}^{L,N} \mathcal{D}_{MN}^{(L)}(\Omega) \quad (26)$$

After Wigner function rank separation, and evaluation (with considerable effort, even in *Mathematica*) we get the following system of equations:

$$\left\{ \begin{aligned} \frac{\partial}{\partial t} \hat{r}_{0,0}^{(0)}(t) &= -i \frac{Ax}{5\sqrt{6}} \hat{T}_{2,0} \hat{r}_{0,0}^{(2)}(t) \\ \frac{\partial}{\partial t} \hat{r}_{0,0}^{(2)}(t) &= -i \frac{Ax}{\sqrt{6}} \hat{T}_{2,0} \left( \hat{r}_{0,0}^{(0)}(t) + \frac{2}{7} \hat{r}_{0,0}^{(2)}(t) + \frac{2}{7} \hat{r}_{0,0}^{(4)}(t) \right) - 6D \hat{r}_{0,0}^{(2)}(t) \\ \frac{\partial}{\partial t} \hat{r}_{0,0}^{(4)}(t) &= -i \frac{Ax}{\sqrt{6}} \hat{T}_{2,0} \left( \frac{18}{35} \hat{r}_{0,0}^{(2)}(t) + \frac{20}{77} \hat{r}_{0,0}^{(4)}(t) + \frac{45}{143} \hat{r}_{0,0}^{(6)}(t) \right) - 20D \hat{r}_{0,0}^{(4)}(t) \\ \dots \end{aligned} \right. \quad (27)$$

This is a block-tridiagonal system of differential equations that may be solved using standard numerical methods and also has an analytical solution in terms of a continued fraction expansion. An important feature that guarantees convergence with respect to the  $l$  rank of Wigner functions is the damping term in Equation (25) that is quadratic with respect to that rank. For typical liquid state systems (correlation time of the order of nanoseconds) convergence is achieved around  $l=10$ . However, for calculations close to the solid limit Wigner function ranks way over 100 may in practice be required. Because the dimension of the spatial basis grows cubically with  $l$  and exponentially with the number of spins in the system, astronomical matrix dimension is the primary practical problem of the SLE formalism – typical workstations would normally only cope with the smallest spin systems.