Sodium Spin Dynamics

Chengchuan Wu, Yasmin Blunck, Leigh Johnston

The Sodium Spin System

The purpose of this work is to find the matrix form of the sodium spin dynamics with respect to the RF rotating frame. The dynamics of the density operator $\hat{\rho}$ can be described by the master equation incorporating the Redfield relaxation function $\hat{\hat{\Gamma}}$ [1, 2],

$$\frac{d}{dt}\hat{\rho}(t) = -i[\hat{H}_D, \hat{\rho}(t)] - \hat{\hat{\Gamma}}\left(\hat{\rho}(t) - \hat{\rho}_0\right), \tag{1}$$

where $\hat{\rho}_0$ denotes the density operator at thermal equilibrium and $\hat{H}_D$ denotes the Hamiltonian of deterministic propagation consisting of three terms,

$$\hat{H}_D = \hat{H}_\Delta + \hat{H}_1 + \hat{H}_{QS}. \tag{2}$$

Here, $\hat{H}_\Delta$, $\hat{H}_1$ and $\hat{H}_{QS}$ derive from the effective static magnetic field, the RF field and the time-averaged quadrupolar EFG, respectively.

The relaxation superoperator describes the interaction with the fluctuating quadrupolar Hamiltonian $\hat{H}_{QF}$ [1, 3, 4],

$$\hat{\hat{\Gamma}}\left(\hat{\rho}(t) - \hat{\rho}_0\right) = \int_0^\infty \left[\hat{H}_{QF}(t), \left[\exp\left\{-i\hat{H}_D\tau\right\}\hat{H}_{QF}(t-\tau)\exp\left\{i\hat{H}_D\tau\right\}, \hat{\rho}(t) - \hat{\rho}_0\right]\right] d\tau. \tag{3}$$

The irreducible spherical tensor operators (ISTO) set is selected as the basis for the matrix representation of Eq.1. The ISTO basis consists of orthonormal components,

$$\left\{\hat{T}_{l0}, \hat{T}_{lm}(a), \hat{T}_{lm}(s) \,|\, l = 0, 1, 2, 3,\ m = 1, \ldots, l\right\}, \tag{4}$$

where l and m are the rank and coherence order of the tensor operator, respectively [5]. Under this treatment, $\hat{T}_{11}(a)$, $\hat{T}_{11}(s)$ and $\hat{T}_{10}$ are proportional to the x-, y- and z-angular momentum operators, respectively, while T_{00} is the identity operator. Given the assumption that the spin ensemble is isolated, T_{00} has no contribution to the spin dynamics and therefore can be omitted [3], forming the reduced basis,

$$\left\{\hat{T}_{10}, \hat{T}_{11}(a), \hat{T}_{11}(s), \hat{T}_{20}, \hat{T}_{21}(a), \hat{T}_{21}(s), \hat{T}_{22}(a), \hat{T}_{22}(s), \hat{T}_{30}, \hat{T}_{31}(a), \hat{T}_{31}(s), \hat{T}_{32}(a), \hat{T}_{32}(s), \hat{T}_{33}(a), \hat{T}_{33}(s)\right\}. \tag{5}$$

Note that we use two forms of ISTO bases interchangeably; the relationship between the native ISTOs, $\{\hat{T}_{lm} \;|\, l = 1,\ 2,\ 3,\ m = -l, \ldots, l\}$, and the symmetric (s) and antisymmetric (a) ISTOs is given by [3]:

$$\hat{T}_{lm}(s) = \frac{1}{\sqrt{2}}\left(\hat{T}_{l-m} + \hat{T}_{lm}\right) \tag{6a}$$

$$\hat{T}_{lm}(a) = \frac{1}{\sqrt{2}}\left(\hat{T}_{l-m} - \hat{T}_{lm}\right). \tag{6b}$$

With the basis defined as above, the commutation and the relaxation superoperator acting on $\hat{\rho}$ can be represented as matrices $\mathbf{D}$ and $\mathbf{R}$ applied to $\mathbf{P}$, the vector representation of $\hat{\rho}$. The equilibrium-state, $\hat{\rho}_0$, gives rise to an offset term, **C**. Therefore Eq.1 can be written in a form akin to the Bloch equation, as

$$
\begin{aligned}
\frac{d}{dt}\mathbf{P} &= (\mathbf{D} + \mathbf{R})\,\mathbf{P} + \mathbf{C} \\
&= \mathbf{L}\mathbf{P} + \mathbf{C}.
\end{aligned}
\tag{7}
$$

Here, **L** is the 15x15 system matrix of the SBE. The matrix **L** is parameterised by RF amplitude (nutation frequency), $\omega_1(t)$, the initial RF phase, ϕ_0 with reference to the x′-axis, off-resonance frequency, $\omega_\Delta(t)$, time-average residual quadrupolar frequency, ω_Q, and spectral densities, J_0, J_1 and J_2. The following sections are to derive the elements of **L** and **C**.

$$
\left[\begin{array}{ccccccccccccccc}
-\frac{2J_1}{5}-\frac{8J_2}{5} & -\omega_1(t)\sin\phi_0 & -i\omega_1(t)\cos\phi_0 & 0 & 0 & 0 & 0 & 0 & -\frac{4J_1}{5}+\frac{4J_2}{5} & 0 & 0 & 0 & 0 & 0 & 0 \\
\omega_1(t)\sin\phi_0 & -\frac{3J_0}{5}-J_1-\frac{2J_2}{5} & i\omega_\Delta(t) & 0 & 0 & i\sqrt{3/5}\,\omega_Q & 0 & 0 & 0 & -\frac{\sqrt{6}J_0}{5}+\frac{\sqrt{6}J_2}{5} & 0 & 0 & 0 & 0 & 0 \\
-i\omega_1(t)\cos\phi_0 & i\omega_\Delta(t) & -\frac{3J_0}{5}-J_1-\frac{2J_2}{5} & 0 & i\sqrt{3/5}\,\omega_Q & 0 & 0 & 0 & 0 & 0 & -\frac{\sqrt{6}J_0}{5}+\frac{\sqrt{6}J_2}{5} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -2J_1-2J_2 & -\sqrt{3}\omega_1(t)\sin\phi_0 & -i\sqrt{3}\omega_1(t)\cos\phi_0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & i\sqrt{3/5}\,\omega_Q & \sqrt{3}\omega_1(t)\sin\phi_0 & -J_0-J_1-2J_2 & i\omega_\Delta(t) & -i\omega_1(t)\cos\phi_0 & -\omega_1(t)\sin\phi_0 & 0 & 0 & i\sqrt{2/5}\,\omega_Q & 0 & 0 & 0 & 0 \\
0 & i\sqrt{3/5}\,\omega_Q & 0 & -i\sqrt{3}\omega_1(t)\cos\phi_0 & i\omega_\Delta(t) & -J_0-J_1-2J_2 & -\omega_1(t)\sin\phi_0 & -i\omega_1(t)\cos\phi_0 & 0 & i\sqrt{2/5}\,\omega_Q & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -i\omega_1(t)\cos\phi_0 & \omega_1(t)\sin\phi_0 & -J_0-2J_1-J_2 & i2\omega_\Delta(t) & 0 & 0 & 0 & 0 & i\omega_Q & 0 & 0 \\
0 & 0 & 0 & 0 & \omega_1(t)\sin\phi_0 & -i\omega_1(t)\cos\phi_0 & i2\omega_\Delta(t) & -J_0-2J_1-J_2 & 0 & 0 & 0 & i\omega_Q & 0 & 0 & 0 \\
-\frac{4J_1}{5}+\frac{4J_2}{5} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{8J_1}{5}-\frac{2J_2}{5} & -\sqrt{6}\omega_1(t)\sin\phi_0 & -i\sqrt{6}\omega_1(t)\cos\phi_0 & 0 & 0 & 0 & 0 \\
0 & -\frac{\sqrt{6}J_0}{5}+\frac{\sqrt{6}J_2}{5} & 0 & 0 & 0 & i\sqrt{2/5}\,\omega_Q & 0 & 0 & \sqrt{6}\omega_1(t)\sin\phi_0 & -\frac{2J_0}{5}-J_1-\frac{3J_2}{5} & i\omega_\Delta(t) & -i\sqrt{\frac{5}{2}}\omega_1(t)\cos\phi_0 & -\sqrt{\frac{5}{2}}\omega_1(t)\sin\phi_0 & 0 & 0 \\
0 & 0 & -\frac{\sqrt{6}J_0}{5}+\frac{\sqrt{6}J_2}{5} & 0 & i\sqrt{2/5}\,\omega_Q & 0 & 0 & 0 & -i\sqrt{6}\omega_1(t)\cos\phi_0 & i\omega_\Delta(t) & -\frac{2J_0}{5}-J_1-\frac{3J_2}{5} & -\sqrt{\frac{5}{2}}\omega_1(t)\sin\phi_0 & -i\sqrt{\frac{5}{2}}\omega_1(t)\cos\phi_0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & i\omega_Q & 0 & -i\sqrt{\frac{5}{2}}\omega_1(t)\cos\phi_0 & \sqrt{\frac{5}{2}}\omega_1(t)\sin\phi_0 & -J_0-J_2 & i2\omega_\Delta(t) & -i\sqrt{\frac{3}{2}}\omega_1(t)\cos\phi_0 & -\sqrt{\frac{3}{2}}\omega_1(t)\sin\phi_0 \\
0 & 0 & 0 & 0 & 0 & 0 & i\omega_Q & 0 & 0 & \sqrt{\frac{5}{2}}\omega_1(t)\sin\phi_0 & -i\sqrt{\frac{5}{2}}\omega_1(t)\cos\phi_0 & i2\omega_\Delta(t) & -J_0-J_2 & -\sqrt{\frac{3}{2}}\omega_1(t)\sin\phi_0 & -i\sqrt{\frac{3}{2}}\omega_1(t)\cos\phi_0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -i\sqrt{\frac{3}{2}}\omega_1(t)\cos\phi_0 & \sqrt{\frac{3}{2}}\omega_1(t)\sin\phi_0 & -J_1-J_2 & i3\omega_\Delta(t) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{\frac{3}{2}}\omega_1(t)\sin\phi_0 & -i\sqrt{\frac{3}{2}}\omega_1(t)\cos\phi_0 & i3\omega_\Delta(t) & -J_1-J_2
\end{array}\right]
$$

Figure 1: The Sodium Bloch Equation system matrix, **L**, colour-coded to indicate source of terms: Red-shaded entries are associated with RF excitation; Yellow-shaded entries are off-resonance terms; Green-shaded terms are associated with residual quadrupolar oscillation; Blue-shaded terms are associated with the fluctuating quadrupolar interaction. (color should be used for this figure in print)

The Deterministic Matrix D

The generator, **D**, of the system matrix **L** in (7) gives rise to deterministic spin dynamics, i.e. nutation, free precession and quadrupolar coupling. By definition, the commutator is

$$
\begin{aligned}
\mathbf{D} &\triangleq -i[\hat{H}_D, \mathbf{E}] \\
&= -i\left[\sqrt{5}\omega_\Delta \hat{T}_{10} + \sqrt{5}\omega_1 e^{i\phi_0}\hat{T}_{11}(a) + \omega_Q \hat{T}_{20}, \mathbf{E}\right] \\
&= -i\left[\sqrt{5}\omega_\Delta \hat{T}_{10}, \mathbf{E}\right] - i\left[\sqrt{5}\omega_1 e^{i\phi_0}\hat{T}_{11}(a), \mathbf{E}\right] - i\left[\omega_Q \hat{T}_{20}, \mathbf{E}\right],
\end{aligned}
\tag{8}
$$

where **E** is the identity matrix and is equivalent to the sum of the ISTOs. The matrix form **D** results from expanding the commutators using commutation laws [3, 6, 7].

The non-zero elements of **D** are shaded yellow, red and green in Fig. 1, corresponding to off-resonance precession, nutation and static quadrupolar coupling, respectively.

The Relaxation Matrix R

With $\hat{H}_{QF}$ expressed in the tensor operator basis, the relaxation superoperator has the form [8]

$$\hat{\hat{\Gamma}}(\hat{\rho}) = -\int_0^\infty \sum_{m=-2}^{2} \left[\hat{T}_{2m}, \left[e^{-i\hat{H}_D\tau}\hat{T}^\dagger_{2m}e^{i\hat{H}_D\tau}, \hat{\rho}\right]\right] \left(\frac{eQ}{\hbar}\right)^2 \langle\left[F^*_{2m}(t) - \left\langle F^*_{2m}\right\rangle\right]\left[F_{2m}(t-\tau) - \langle F_{2m}\rangle\right]\rangle e^{im\omega_r\tau}d\tau, \tag{9}$$

where $\hat{T}^\dagger_{2m} = (-1)^m\hat{T}_{2-m}$, e is the unit electric charge, Q is the quadrupole moment, F_{2m} is the EFG tensor component, ω_r is the frequency of the rotating frame, $\langle\cdot\rangle$ and $*$ denote motion average and complex conjugation, respectively.

The integral in Eq.9 cannot be resolved except in certain cases. If $\hat{H}_D$ is absent, a matrix representation of $\mathbf{R}$ results [3]. Here, We can demonstrate that $\mathbf{R}$ has the same form (blue shaded entries in Fig. 1) given any practical $\hat{H}_D$ for ^{23}Na NMR in biological tissue environments.

Consider the spectral density, $J(\omega)$ [3],

$$\begin{aligned} J(\omega) &= \frac{(2\pi)^2}{20}\frac{\chi^2\tau_c}{1+(\omega\tau_c)^2} \\ &\approx \int_0^\infty \left(\frac{eQ}{\hbar}\right)^2 \langle\left[F^*_{2m}(t) - \left\langle F^*_{2m}\right\rangle\right]\left[F_{2m}(t-\tau) - \langle F_{2m}\rangle\right]\rangle e^{i\omega\tau}d\tau, \end{aligned} \tag{10}$$

where χ is the quadrupolar coupling constant and τ_c is the correlation time.

The term $e^{-i\hat{H}_D\tau}\hat{T}^\dagger_{2m}e^{i\hat{H}_D\tau}$ in Eq.9 represents the evolution of $T^\dagger_{2m}$ under the influence of $\hat{H}_D$. Thus, its dynamic equation is

$$\frac{d}{dt}\mathbf{T} = \mathbf{DT}. \tag{11}$$

The term $e^{-i\hat{H}_D\tau}\hat{T}^\dagger_{2m}e^{i\hat{H}_D\tau}$ is equivalent to the integral of Eq.11 over $[0,\tau]$ with the initial condition $\mathbf{T}(0) = \hat{T}^\dagger_{2m}$. Note that $\mathbf{D}$ is skew-Hermitian. Therefore, it is diagonalisable and the eigenvalues are purely imaginary. Eq.11 can be rewritten as

$$\frac{d}{dt}\mathbf{T} = \mathbf{Q}^{-1}\begin{bmatrix} i\lambda_1 & & \\ & \ddots & \\ & & i\lambda_{15} \end{bmatrix}\mathbf{QT}, \tag{12}$$

where λ_k's are the eigenvalues and $\mathbf{Q}$ is the eigenvector matrix. By defining $\left[q_{1,s}, \ldots, q_{15,s}\right]^\top$ as the s-th column in $\mathbf{Q}$ corresponding to the initial condition such that $\mathbf{T}_s = \hat{T}_{2m}$, we obtain the expression of $e^{-i\hat{H}_D\tau}\hat{T}^\dagger_{2m}e^{i\hat{H}_D\tau}$ in the ISTO basis,

$$\begin{aligned} e^{-i\hat{H}_D\tau}\hat{T}^\dagger_{2m}e^{i\hat{H}_D\tau} &= \mathbf{Q}^{-1}\begin{bmatrix} (-1)^m q_{1,s}e^{i\lambda_1\tau} \\ \vdots \\ (-1)^m q_{15,s}e^{i\lambda_{15}\tau} \end{bmatrix} \\ &= \frac{1}{\det(\mathbf{Q})}\begin{bmatrix} Q_{1,1} & \cdots & Q_{15,1} \\ \vdots & \ddots & \vdots \\ Q_{1,15} & \cdots & Q_{15,15} \end{bmatrix}\begin{bmatrix} (-1)^m q_{1,s}e^{i\lambda_1\tau} \\ \vdots \\ (-1)^m q_{15,s}e^{i\lambda_{15}\tau} \end{bmatrix} \\ &= \frac{1}{\det(\mathbf{Q})}\begin{bmatrix} (-1)^m \sum_k Q_{k,1}q_{k,s}e^{i\lambda_k\tau} \\ \vdots \\ (-1)^m \sum_k Q_{k,15}q_{k,s}e^{i\lambda_k\tau} \end{bmatrix} \\ &= \sum_{l=1}^{3}\sum_{n=-l}^{l}\sum_{k=1}^{15}\alpha_{klmn}e^{i\lambda_k\tau}\hat{T}_{ln}, \end{aligned} \tag{13}$$

where α_{klmn} is introduced to denote the coefficient.

Rearrange and simplify Eq.9 by the following steps:

$$\begin{aligned}
\hat{\hat{\Gamma}}(\hat{\rho}) &= -\sum_{m=-2}^{2}\left[\hat{T}_{2m},\left[\sum_{l,n}\sum_{k}\alpha_{klmn}J(m\omega_r+\lambda_k)\hat{T}_{ln},\hat{\rho}\right]\right] \\
&\approx -\sum_{m=-2}^{2}\left[\hat{T}_{2m},\left[\sum_{l,n}\sum_{k}\alpha_{klmn}J(m\omega_0)\hat{T}_{ln},\hat{\rho}\right]\right] \\
&= -\sum_{m=-2}^{2}\left[\hat{T}_{2m},\left[\sum_{l,n}\sum_{k}\alpha_{klmn}\hat{T}_{ln},\hat{\rho}\right]\right]J(m\omega_r) \\
&= -\sum_{m=-2}^{2}\left[\hat{T}_{2m},\left[\hat{T}_{2m}^{\dagger},\hat{\rho}\right]\right]J(m\omega_0)
\end{aligned} \tag{14}$$

Here, there are two key steps in the derivation. Firstly, the eigenvalues are upper-bounded according to Bendixson's inequality [9]

$$\lambda \leq 15\max\left(|d_{ij}|\right) \tag{15}$$

where d_{ij} are the elements of $\mathbf{D}$ and in the same order of magnitude as ω_1, ω_Δ and ω_Q. Since $\lambda \ll 1/\tau_c$ in biological environments and $\omega_r \approx \omega_0$, we have $J(m\omega_r+\lambda_k) \approx J(m\omega_0)$. Conventionally, $J(m\omega_0)$ is also denoted as J_m.

Secondly, summing the products of elements and cofactors results in [10]

$$\sum_k \alpha_{klmn} = \begin{cases} (-1)^m & \text{when } l = 2 \text{ and } n = m \\ 0 & \text{otherwise} \end{cases} \tag{16}$$

Eq.14 suggests that the effect of $\hat{H}_D$ is negligible in the relaxation process because the interaction occurs on a slow timescale, and can therefore be approximated by the case $\hat{H}_D = 0$. The expression of $\mathbf{R}$ follows from expansion of the double commutator [3].

The Offset C

If thermal equilibrium, $\hat{\rho}_0 = \mathbf{P}(0) = \hat{T}_{10}$, is assumed, the offset can be determined by applying the initial condition $\mathbf{C} = -\mathbf{RP}(0)$, such that

$$\mathbf{C} = \left[\frac{2}{5}J_1 + \frac{8}{5}J_2, 0, 0, 0, 0, 0, 0, 0, \frac{4}{5}J_1 - \frac{4}{5}J_2, 0, 0, 0, 0, 0, 0\right]^\top. \tag{17}$$

With these definitions of $\mathbf{L}$ and $\mathbf{C}$, the SBE as defined by Eq. 7 is fully described.

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