Fast and accurate MAS-DNP simulations of large spin ensemble

Frédéric Mentink-Vigier,ab Shimon Vega,c Gaël De Paëpe*ab
a Univ. Grenoble Alpes, INAC, MEM, F-38000 Grenoble, France. E-mail: gael.depaepe@cea.fr
b CEA, INAC, MEM, F-38000 Grenoble, France and
c Weizmann institute of Science, Rehovot, Israel
(Dated:)

I. THE ROTOR-EVENT ANALYSIS

For the purpose of clarity, part of the main manuscript is repeated here in order to help the reader. As explained previously, high magnetic field MAS-DNP simulations can be efficiently computed in the μw rotating frame as described in [1–3]. The corresponding Hamiltonian for two electrons (with indices $i, i' = a, b$) and one nucleus (with indices $j = 1$) can be written:

$$\begin{aligned}\widehat{H}(t) &= \widehat{H}_0(t) + \widehat{H}_{\mu\mathrm{w}} \\ \widehat{H}_0(t) &= \widehat{H}_{\mathrm{Z}}(t) + \widehat{H}_{\mathrm{HF}}(t) + \widehat{H}_{\mathrm{J}} + \widehat{H}_{\mathrm{Dip}}(t) + \widehat{H}_{\mathrm{d}}(t),\end{aligned} \tag{1}$$

and the terms are:

$$\begin{aligned}\widehat{H}_{\mathrm{Z}}(t) &= (\omega_a(t) - \omega_{\mu\mathrm{w}})\widehat{S}_{a,z} + (\omega_b(t) - \omega_{\mu\mathrm{w}})\widehat{S}_{b,z} - \omega_n\widehat{I}_{n,z} \\ \widehat{H}_{\mathrm{HF}}(t) &= A_z(t)\widehat{S}_{a,z}\widehat{I}_{n,z} + \frac{1}{2}(A^+(t)\widehat{S}_{a,z}\widehat{I}_n^+ + A^-(t)\widehat{S}_{a,z}\widehat{I}_n^-) \\ \widehat{H}_{\mu\mathrm{w}} &= \omega_1(\widehat{S}_{a,x} + \widehat{S}_{b,x}) \\ \widehat{H}_{\mathrm{J}} &= -2J_{a,b}(\widehat{S}_{a,z}\widehat{S}_{b,z} + \frac{1}{2}(\widehat{S}_a^+\widehat{S}_b^- + \widehat{S}_a^-\widehat{S}_b^+)) \\ \widehat{H}_{\mathrm{Dip}}(t) &= D_{a,b}(t)(2\widehat{S}_{a,z}\widehat{S}_{b,z} - \frac{1}{2}(\widehat{S}_a^+\widehat{S}_b^- + \widehat{S}_a^-\widehat{S}_b^+))\end{aligned} \tag{2}$$

The time propagation of this three-spin system with two electrons with $S = 1/2$ and a nucleus with $I = 1/2$ can be evaluated by solving the Master equation (Liouville-von Neumann (L-vN) equation including relaxation) for its spin density operator. In operator space this equation determines the time evolution of the expectation values of a full set of independent operators $\widehat{S}^{(m)}$ that are required to decompose the spin density matrix $\widehat{\rho}(t)$. For the three spin 1/2 problem, the dimension of $\widehat{\rho}(t)$ is $2^3 \times 2^3 = 64$, and requires 64 independent operators ($m \in [\![1, 64]\!]$) to decompose this matrix in operator form on the basis of $\widehat{S}^{(m)}$ spin operators

$$\widehat{\rho}(t) = \sum_{m=1}^{64} 2s^{(m)}(t)\widehat{S}^{(m)} \tag{3}$$

We define here the vector $\sigma(t)$ composed of all coefficients $\sigma_m(t) = s^{(m)}(t)$ that are equal to the expectation values $\langle\widehat{S}^{(m)}\rangle(t) = s^{(m)}(t)$, with $m \in [\![1, 64]\!]$, when assuming that $\mathrm{Tr}(\widehat{S}^{(m)2}) = 1/2$. The components of the Liouvillian $\widehat{\widehat{L}}$ operating on the 64 expectation values are thus 64×64 matrix

$$\frac{d}{dt}\sigma(t) = \widehat{\widehat{L}}_H(t)\sigma(t) + \widehat{\widehat{R}}_2\sigma(t) + \widehat{\widehat{R}}_1(\sigma(t) - \sigma^{eq}) \tag{4}$$

The σ^{eq} vector is composed of all $s_{eq}^{(m)}$'s of the thermal equilibrium $\widehat{\rho}_{eq}$ in the laboratory frame. The elements of $\widehat{\widehat{L}}_H$ are determined by the matrix elements of the Hamiltonian and $\widehat{\widehat{R}}_2$ and $\widehat{\widehat{R}}_1$ by the relaxation rates responsible for the decay of coefficients of the off-diagonal operators and the return of the coefficients of the diagonal operators the to the thermal equilibrium values $s_{eq}^{(m)}$, respectively. The large dimension, and the time dependence of $\widehat{\widehat{L}}$ are the main cause of the long time span necessary to solve the master equation. The present work aims at reducing

the size of the $\sigma(t)$ vector and thereby the dimension of $\hat{\hat{L}}$ in an effort to shorten significantly the computational time.

In earlier studies we accomplished the evaluation of the time dependence of $\hat{\rho}$ by evaluating the evolution operators of a single rotor period by subdividing this time period in a large number of small time intervals $(\kappa-1)\delta t$ to $\kappa\delta t$ with $\kappa = [\![1, K]\!]$ and $t_r = K\delta t$ the length of the rotor period. During these calculations we represented the density operator by a state vector composed of its elements and $\hat{\hat{L}}(t)$ in the master equation was defined accordingly. To determine the spin evolution, during each time interval we constructed the constant operator $\hat{\hat{L}}_\kappa = \hat{\hat{L}}(\kappa\delta t)$ derived from $\hat{H}(\kappa\delta t)$ and calculated the evolution operator $\hat{\hat{U}}_\kappa = \exp(\hat{\hat{L}}_\kappa\delta t)$. $\hat{\hat{U}}_\kappa$ is determining the propagation of $\hat{\rho}$ via $\hat{\rho}(\kappa\delta t) = \hat{\hat{U}}_\kappa\hat{\rho}((\kappa-1)\delta t)$. During sample rotation the evolution during each interval can be characterized by the action of the four possible rotor events happening during the interval and the relaxation mechanisms.

In the following sections we derive expressions for the $\hat{\hat{L}}_\kappa$ and $\hat{\hat{U}}_\kappa$ operators corresponding to the rotor events after possible reduction of the dimensionality of $\sigma(t)$. In the next discussion we assume that two or more rotor-events do not occur at the same time. During the derivations we will use the fact that each event involves a crossing of only two energy levels and that therefore a reduction of the dimensions of the the $\hat{\hat{L}}_\kappa$ and $\hat{\hat{U}}_\kappa$ matrices can be accomplished.

A. The Bloch equation for two anti-crossing energy levels.

At first we describe the evolution of a system with two spin states $|1\rangle$ and $|2\rangle$ that cross at a time $t_\times$. When we define the energy difference between the states crossing two states by $\Delta\omega_{12}(t)$ then at time $t_\times$, $\Delta\omega_{12}(t_\times) = 0$. When in addition the two levels are coupled via an interaction of strength $\xi_{12}(t)$ then the effective Hamiltonian determining the spin evolution of the two-level system has the form

$$\hat{H}_{12}(t) = \frac{1}{2}\begin{pmatrix} \Delta\omega_{12}(t) & \xi_{12}(t) \\ \xi_{12}^*(t) & -\Delta\omega_{12}(t) \end{pmatrix} \tag{5}$$

where in general $\xi_{12}(t) = 1/2(\xi_x^{12} - i\xi_y^{12})$. Then this Hamiltonian can expressed in operator form as

$$\hat{H}_{12}(t) = \Delta\omega_{12}(t)\hat{S}_z^{12} + \xi_x^{12}(t)\hat{S}_x^{12} + \xi_y^{12}(t)\hat{S}_y^{12}, \tag{6}$$

where $\hat{S}_x^{12}, \hat{S}_y^{12}, \hat{S}_z^{12}$ are the fictitious spin-1/2 operators corresponding to the transition $|1\rangle - |2\rangle$. In Liouville space $\hat{\hat{L}}_H(t)$, $\hat{\hat{R}}_1$ and $\hat{\hat{R}}_2$ matrices can be derived that operate on the state vector defined by the coefficients $\{s_z^{12}(t), s_y^{12}(t), s_x^{12}(t)\}$ of the spin density operator $\hat{\rho}(t) = \sum_{p=x,y,z} s_p^{12}(t)\hat{S}_p^{12} + s_0^{12}\hat{S}_0^{12}$. The form of these operators are

$$\hat{\hat{L}}_H^{1,2}(t) = \begin{bmatrix} 0 & -\xi_x^{12}(t) & \xi_y^{12}(t) \\ \xi_x^{12}(t) & 0 & -\Delta\omega^{12}(t) \\ -\xi_y^{12}(t) & \Delta\omega^{12}(t) & 0 \end{bmatrix}; \quad \hat{\hat{R}}_2 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & -1/T_2 & 0 \\ 0 & 0 & -1/T_2 \end{bmatrix}; \quad \hat{\hat{R}}_1 = \begin{bmatrix} -1/T_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{7}$$

Insertion of these operators in the master equation in Eq. 2 results in the well-known Bloch equations. Levit and Di Bari as well as Levante and Ernst [4, 5] have suggested to extend the $\sigma(t)$ vector by choosing a constant coefficient $s_0 = 1$ of the unit operator $\hat{S}_0^{12}$ in order to transform the master rate equation from a in-homogeneous to a homogeneous form. In that case the Bloch operator $\hat{\hat{L}}_B(t) = \hat{\hat{L}}_H^{1,2}(t) + \hat{\hat{R}}_1 + \hat{\hat{R}}_2$ becomes a 4×4 matrix and the master equation gets the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} 1 \\ s_z^{12} \\ s_y^{12} \\ s_x^{12} \end{bmatrix}(t) = \begin{bmatrix} 0 & 0 & 0 & 0 \\ s_z^{12,eq}/T_1 & -1/T_1 & -\xi_x^{12}(t) & \xi_y^{12}(t) \\ 0 & \xi_x^{12}(t) & -1/T_2 & -\Delta\omega^{12}(t) \\ 0 & -\xi_y^{12}(t) & \Delta\omega^{12}(t) & -1/T_2 \end{bmatrix}\begin{bmatrix} 1 \\ s_z^{12} \\ s_y^{12} \\ s_x^{12} \end{bmatrix}(t) \tag{8}$$

where we assumed that $\hat{\rho}^{eq} = 2s_z^{12,eq}\hat{S}_z^{12}$. The solution of this equation provides the spin evolution of a two-level system in the form of the time dependence of the $s_p(t)$, $p = x, y, z$, vector elements. This solution depends on all Hamiltonian parameters, and in particular on the value $\xi^{12}(t_\times)$ around $t_\times$ for which $\Delta\omega^{12}(t_\times) = 0$. The time dependence of the $\sigma(t)$ vector can be obtained by step integration of the master equation. Defining the boundaries

of the time intervals of the integration by $t_\kappa = \kappa\delta t$ with $\kappa \in [\![1, K]\!]$ and $\delta t = t_r/K$, the propagator $\widehat{\widehat{U}}(0 : t_k)$ responsible for the spin evolution from $t = 0$ to t_k can be calculated as:

$$\widehat{\widehat{U}}_{\mathrm{B},}(0 : t_k) = \prod_{\kappa=1}^{k} \widehat{\widehat{U}}_{\mathrm{B},\kappa} \; ; \qquad \widehat{\widehat{U}}_{\mathrm{B},\kappa} = \exp(\widehat{\widehat{L}}_B(t_\kappa)\delta t) \tag{9}$$

The $\widehat{\widehat{R}}_2$ causes a decay of the coherences $s_x^{12}(t)$ and $s_y^{12}(t)$ and indirectly influences the time evolution of $s_z^{12}(t)$ towards its equilibrium value.

B. The Landau - Zener solution of the two level anti-crossing event.

Following notations introduced in section 2 B, we are now addressing the case of rotor events for which $\omega_{1,2}^2 \ll 1$. In such cases, the jump time associated with the transition is typically smaller than 1 μs. As a consequence, the electronic T_2 relaxation time can easily be longer than the duration of the crossing, and thus its influence on the spin evolution conveniently ignored. In that case we can rely on the Landau-Zener formula for the change of the difference between the populations of $|1\rangle$ and $|2\rangle$, expressed by the value of $s_z^{12}(t)$, before and after the crossing $t_\times$. When $t_\times$ is included in the time step interval $[t_{\kappa-1}, t_\kappa]$, we can define a $\widehat{\widehat{U}}_{\mathrm{LZ},\kappa}$ propagator based on this formalism that act on the elements of the state vector, assuming that $s_x^{12}(t_{\kappa-1}) = s_y^{12}(t_{\kappa-1}) = 0$, as

$$\begin{aligned} s_x^{12}(t_{\kappa-1}^+) &= \widehat{\widehat{U}}_{\mathrm{LZ},\kappa} s_x^{12}(t_{\kappa-1}) = 0 \\ s_y^{12}(t_{\kappa-1}^+) &= \widehat{\widehat{U}}_{\mathrm{LZ},\kappa} s_y^{12}(t_{\kappa-1}) = 0 \\ s_z^{12}(t_{\kappa-1}^+) &= \widehat{\widehat{U}}_{\mathrm{LZ},\kappa} s_z^{12}(t_{\kappa-1}) = [1 - 2\epsilon_\kappa^{12}] s_z^{12}(t_{\kappa-1}) \end{aligned} \qquad \text{with} \quad \epsilon_\kappa^{12} = 1 - \exp\left[\frac{-\pi|\xi_{12}(t_{\kappa-1})|^2}{2|\frac{\mathrm{d}}{\mathrm{d}t}\Delta\omega_{12}|_{t_{\kappa-1}}}\right]$$

where we rely on the fact that $t_{\kappa-1} \cong t_\times$ and $t_{\kappa-1}^+$ is the time just after the event. In the case we can rely on the Landau-Zener formalism, $\widehat{\widehat{U}}_{\mathrm{B},\kappa}$ can be approximated by the single element operator $\widehat{\widehat{U}}_{\mathrm{LZ},\kappa}$ operating on $s_z^{12}(t_{\kappa-1})$ times the longitudinal relaxation propagator during the time interval $[t_{\kappa-1}, t_\kappa]$. With this approach it is possible to account for the longitudinal relaxation by working with the $\{1, s_z^{12}\}$ coefficients. The propagator for this time interval containing a level crossing event equals then

$$\widehat{\widehat{U}}_k = \exp(\widehat{\widehat{R}}_1\delta t) \times \widehat{\widehat{U}}_{\mathrm{LZ},\kappa} = \begin{bmatrix} 0 & 0 \\ [s_z^{12,eq}(1 - e^{-\delta t/T_1})] & [e^{-\delta t/T_1}(1 - 2\epsilon_\kappa^{12})] \end{bmatrix}$$

where

$$\widehat{\widehat{R}}_1(t) = \begin{bmatrix} 0 & 0 \\ s_z^{12,eq}(t)/T_1 & -1/T_1 \end{bmatrix} \quad ; \quad \mathrm{e}^{R_1\delta t} = \begin{bmatrix} 0 & 0 \\ s_z^{12,eq}(1 - e^{-\delta t/T_1}) & e^{-\delta t/T_1} \end{bmatrix} \quad \text{and} \quad \widehat{\widehat{U}}_{\mathrm{LZ},\kappa} = \begin{bmatrix} 1 & 0 \\ 0 & 1 - 2\epsilon_\kappa^{12} \end{bmatrix}.$$

In the following sections we will determine the necessary $\widehat{S}^{(m)}$ operators (or $s^{(m)}$ coefficients) and which of the two approaches, the Bloch type or the Landau-Zener propagation, are required to present the four rotor-events in our thee-spin system and shorten the simulation's duration.

1. *The μw rotor events*

Let us assume that the electron a in the $\{e_a - e_b - n\}$ spin system undergoes a μw rotor-event at time $t_\times$. For simplicity we further assume that the four events, where the levels $|\beta_a\chi_b\chi_n\rangle$ and $|\alpha_a\chi_b\chi_n\rangle$ cross with $\chi = \alpha, \beta$, occur at the same moment $t_\times$. This is indeed the case if we ignore all anisotropic time dependent hyperfine and dipolar and J interactions in the spin Hamiltonian. Such assumption appears reasonable since these interactions are usually smaller than the g-tensor anisotropies. In the μw rotating frame the Hamiltonian can then be written:

$$\widehat{H}_{\mu\mathrm{w}}(t) = (\omega_a(t) - \omega_{\mu\mathrm{w}})\widehat{S}_{a,z} + (\omega_b(t) - \omega_{\mu\mathrm{w}})\widehat{S}_{b,z} - \omega_n\widehat{I}_{n,z} + \omega_1(\widehat{S}_{a,x} + \widehat{S}_{b,x})$$

With this assumption the four simultaneous μw rotor events happen when $\Delta\omega_a(t_\times) = (\omega_a(t_\times) - \omega_{\mu\mathrm{w}}) = 0$. These four crossings can be described by a Liouville space vector $\sigma(t)$ composed of the following elements

$\{s_{a,z}(t), s_{a,y}(t), s_{a,x}(t)\}$. In the matrix representation of $\widehat{H}_{\mu\mathrm{w}}(t)$, the Liouvillian can be written:

$$\widehat{\widehat{L}}_H^{a,\mu\mathrm{w}}(t) = \begin{bmatrix} 0 & -\omega_1 & 0 \\ \omega_1 & 0 & -\Delta\omega_a(t) \\ 0 & \Delta\omega_a(t) & 0 \end{bmatrix} \qquad \text{with } \sigma_{a,\mu\mathrm{w}}(t) = \begin{bmatrix} s_{a,z} \\ s_{a,y} \\ s_{a,x} \end{bmatrix}(t) \tag{10}$$

To obtain an homogeneous master equation, $s_0 = 1$ can be added (see section A for details) in order to introduce both transverse and longitudinal relaxation. This Bloch-type Liouvillian has thus the following form in the basis set $\{\widehat{E}, \widehat{S}_{a,z}, \widehat{S}_{a,y}, \widehat{S}_{a,x}\}$:

$$\widehat{\widehat{L}}_B^{a,\mu\mathrm{w}}(t) = \begin{bmatrix} 0 & 0 & 0 & 0 \\ s_{a,z}^{eq}(t)/T_{1,a} & -1/T_{1,a} & -\omega_1 & 0 \\ 0 & \omega_1 & -1/T_{2,a} & -\Delta\omega_a(t) \\ 0 & 0 & \Delta\omega_a(t) & -1/T_{2,a} \end{bmatrix} \qquad \text{with } \sigma_{a,\mu\mathrm{w}}(t) = \begin{bmatrix} 1 \\ s_{a,z} \\ s_{a,y} \\ s_{a,x} \end{bmatrix}(t) \tag{11}$$

and with

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{a,\mu\mathrm{w}}(t) = \widehat{\widehat{L}}_B^{a,\mu\mathrm{w}}(t)\sigma_{a,\mu\mathrm{w}}(t)$$

The propagator of the κ^{th} time interval, $\widehat{\widehat{U}}_{\mathrm{B},a,\kappa}^{,\mu\mathrm{w}} = \exp(\widehat{\widehat{L}}_B^{a,\mu\mathrm{w}}(t_\kappa)\delta t)$, can be straightforwardly calculated and applied on the four elements of $\sigma_{a,\mu\mathrm{w}}(t)$. In cases where the electron $T_{a,2}^e$ is long enough, e.g. at low temperatures, or ω_1 is weak enough and the μw event happens during an interval κ we can apply the Landau-Zener (LZ) formalism and use the 2×2, for both electron a and b, $\widehat{\widehat{U}}_{\mathrm{LZ},\kappa}^{,\mu\mathrm{w}}$ evolution operator

$$\begin{bmatrix} s_{a,z} \\ s_{b,z} \end{bmatrix}(t_\kappa^+) = \widehat{\widehat{U}}_{\mathrm{LZ},\kappa}^{,\mu\mathrm{w}} \begin{bmatrix} s_{a,z} \\ s_{b,z} \end{bmatrix}(t_{\kappa-1}) = \begin{bmatrix} 1-2\epsilon_\kappa^{a,\mu\mathrm{w}} & 0 \\ 0 & 1-2\epsilon_\kappa^{b,\mu\mathrm{w}]} \end{bmatrix} \begin{bmatrix} s_{a,z} \\ s_{b,z} \end{bmatrix}(t_\kappa)$$

with

$$\epsilon_\kappa^{a,\mu\mathrm{w}} = 1 - e^{-\pi|\omega_1|^2/[2(\mathrm{d}/\mathrm{d}t)\Delta\omega_a]_{t_{\kappa-1}}} \text{ if } \mu\mathrm{w} \text{ crossing, or } = 0 \text{ if no crossing}$$
$$\epsilon_\kappa^{b,\mu\mathrm{w}} = 1 - e^{-\pi|\omega_1|^2/[2(\mathrm{d}/\mathrm{d}t)\Delta\omega_b]_{t_{\kappa-1}}} \text{ if } \mu\mathrm{w} \text{ crossing, or } = 0 \text{ if no crossing}$$

The relaxation can be included here as well by introducing the unity operator and in that case

$$\begin{aligned} \begin{bmatrix} 1 \\ s_{a,z} \\ s_{b,z} \end{bmatrix}(t_\kappa) &= \exp(\widehat{\widehat{R}}_1\delta t)\widehat{\widehat{U}}_{\mathrm{LZ},\kappa}^{\mu\mathrm{w}} \begin{bmatrix} 1 \\ s_{a,z} \\ s_{b,z} \end{bmatrix}(t_{\kappa-1}) \\ &= \begin{bmatrix} 0 & 0 & 0 \\ s_a^{eq}(1-e^{-\delta t/T_{1,a}}) & e^{-\delta t/T_{1,a}} & 0 \\ s_b^{eq}(1-e^{-\delta t/T_{1,b}}) & 0 & e^{-\delta t/T_{1,b}} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 1 & 1-2\epsilon_\kappa^{a,\mu\mathrm{w}} & 0 \\ 0 & 0 & 1-2\epsilon_\kappa^{b,\mu\mathrm{w}]} \end{bmatrix} \begin{bmatrix} 1 \\ s_{a,z} \\ s_{b,z} \end{bmatrix}(t_{\kappa-1}) \end{aligned}$$

Consequently, combining both types of μw rotor events in our Bloch type of calculations requires an extension of the necessary coefficient of $\sigma_{\mu\mathrm{w}}(t)$ to $\{s_{a,z}(t), s_{a,y}(t), s_{a,x}(t), s_{b,z}(t), s_{b,y}(t), s_{b,x}(t)\}$. With this manifold of coefficients the Liouville matrix gets a dimension 6×6 (or 7×7 with relaxation). When the LZ approach is sufficient to describe the μw rotor-events, the dimension of the propagators should be extended to 2×2 (or 3×3 with relaxation).

2. The dipolar-J rotor-events

The D-J rotor-events occur when two resonant frequencies of electrons a and b become equal $\omega_a(t_k) = \omega_b(t_k)$. Then the levels $|\alpha_a\beta_b, \chi_n\rangle$ and $|\beta_a\alpha_b\chi_n\rangle$ anti-cross when experiencing a dipolar and/or spin exchange coupling

(D-J), due to the off-diagonal element. For an isolated D/J event the Hamiltonian can be written as

$$\begin{aligned}\widehat{H}_{\text{D-J}}(t) &= (\omega_a(t)-\omega_{\mu\text{w}})\widehat{S}_{a,z}+(\omega_b(t)-\omega_{\mu\text{w}})\widehat{S}_{b,z}-\omega_n\widehat{I}_{n,z}\\ &\quad+(D_{ab}(t)-J_{ab})(2\widehat{S}_{a,z}\widehat{S}_{b,z}-1)+1/2(2J_{ab}+D_{ab}(t))(\widehat{S}_a^+\widehat{S}_b^-+\widehat{S}_a^-\widehat{S}_b^+)\\ &= 1/2(\omega_a(t)+\omega_b(t)-2\omega_{\mu w})(\widehat{S}_{z,a}+\widehat{S}_{z,b})+(D_{ab}(t)-J_{ab})(2\widehat{S}_{a,z}\widehat{S}_{b,z}-1)\\ &\quad+\Delta\omega_{ab}\widehat{S}_{\text{ZQ},z}+(2J_{ab}+D_{ab}(t))\widehat{S}_{\text{ZQ},x}-\omega_n\widehat{I}_{n,z}\end{aligned}$$

where $\Delta\omega_{ab}=1/2(\omega_a(t)-\omega_b(t))$ and $\widehat{S}_{\text{ZQ},z}=1/2(\widehat{S}_{a,z}-\widehat{S}_{b,z})$ and $\widehat{S}_{\text{ZQ},x}=1/2(\widehat{S}_a^+\widehat{S}_b^-+\widehat{S}_a^-\widehat{S}_b^+)$. Ignoring the hyperfine coupling, at the time of a D-J rotor-event two two-levels anti-crossings happen simultaneously for $\chi_n=\alpha_n,\beta_n$. These events can be described using the three fictitious spin-half operators, known as the electron zero-quantum operators describing the $|\alpha_a\beta_b,\chi_n\rangle$ - $|\beta_a\alpha_b\chi_n\rangle$ transitions:

$$\begin{aligned}\widehat{S}_{\text{ZQ},x}&=1/2(\widehat{S}_a^+\widehat{S}_b^-+\widehat{S}_a^-\widehat{S}_b^+)\\ \widehat{S}_{\text{ZQ},y}&=-i/2(\widehat{S}_a^+\widehat{S}_b^--\widehat{S}_a^-\widehat{S}_b^+)\\ \widehat{S}_{\text{ZQ},z}&=1/2(\widehat{S}_{a,z}-\widehat{S}_{b,z})\end{aligned}$$

The evolution of the $\sigma_{\text{D-J}}(t)$ vector during these events can be fully described by following the time dependence of the coefficients $\{s_{\text{ZQ},z}s_{\text{ZQ},y},s_{\text{ZQ},x}\}$ of these operators only. We also define the double quantum operator $\widehat{S}_{\text{DQ},z}=\frac{1}{2}(\widehat{S}_{a,z}+\widehat{S}_{b,z})$, and during the D-J event the $s_{\text{ZQ},z}$ gets modified while the coefficient $s_{\text{DQ},z}$ is invariant. Thus $\widehat{\widehat{L}}_{\text{H}}^{\text{D-J}}$, without relaxation, in the master equation considering only the elements of the Hamiltonian gets the form in the manifold of $\{s_{\text{DQ},z},s_{\text{ZQ},z},s^{\text{D-J}}_{\text{ZQ},y},s^{\text{D-J}}_{\text{ZQ},x}\}$

$$\frac{\text{d}}{\text{d}t}\begin{bmatrix}s_{\text{DQ},z}\\ s_{\text{ZQ},z}\\ s^{\text{D-J}}_{\text{ZQ},y}\\ s^{\text{D-J}}_{\text{ZQ},x}\end{bmatrix}(t)=\widehat{\widehat{L}}_H^{\text{D-J}}\begin{bmatrix}s_{\text{DQ},z}\\ s_{\text{ZQ},z}\\ s^{\text{D-J}}_{\text{ZQ},y}\\ s^{\text{D-J}}_{\text{ZQ},x}\end{bmatrix}(t)=\begin{bmatrix}0&0&0&0\\ 0&0&-DJ_{ab}(t)&0\\ 0&DJ_{ab}(t)&0&-\Delta\omega_{ab}(t)\\ 0&0&\Delta\omega_{ab}(t)&0\end{bmatrix}\begin{bmatrix}s_{\text{DQ},z}\\ s_{\text{ZQ},z}\\ s^{\text{D-J}}_{\text{ZQ},y}\\ s^{\text{D-J}}_{\text{ZQ},x}\end{bmatrix}(t)$$

where $DJ_{ab}=(D_{ab}+2J_{ab})$ is assumed to be real. To combine with the μw rotor-event, $\widehat{\rho}$ must be re-expressed in the basis that includes $\widehat{S}_{a,z}$ and $\widehat{S}_{b,z}$, and here we use the double quantum z operator to perform a basis change from $\{\widehat{S}_{\text{DQ},z}\widehat{S}_{\text{ZQ},z}\widehat{S}^{\text{D-J}}_{\text{ZQ},y},\widehat{S}^{\text{D-J}}_{\text{ZQ},x}\}$ to the basis $\{\widehat{S}_{a,z},\widehat{S}_{b,z},\widehat{S}^{\text{D-J}}_{\text{ZQ},x}\widehat{S}^{\text{D-J}}_{\text{ZQ},y}\}$ via

$$\begin{bmatrix}s_{a,z}\\ s_{b,z}\\ s^{\text{D-J}}_{\text{ZQ},y}\\ s^{\text{D-J}}_{\text{ZQ},x}\end{bmatrix}=\begin{bmatrix}1/2&1/2&0&0\\ 1/2&-1/2&0&0\\ 0&0&1&0\\ 0&0&0&1\end{bmatrix}\begin{bmatrix}s_{\text{DQ},z}\\ s_{\text{ZQ},z}\\ s^{\text{D-J}}_{\text{ZQ},y}\\ s^{\text{D-J}}_{\text{ZQ},x}\end{bmatrix}. \tag{12}$$

Using this transformation the L-vN equation can be re-written in with the coefficients $\{s_{a,z}s_{b,z},s^{\text{D-J}}_{\text{ZQ},y},s^{\text{D-J}}_{\text{ZQ},x}\}$

$$\frac{\text{d}}{\text{d}t}\begin{bmatrix}s_{a,z}\\ s_{b,z}\\ s^{\text{D-J}}_{\text{ZQ},y}\\ s^{\text{D-J}}_{\text{ZQ},x}\end{bmatrix}(t)=\widehat{\widehat{L}}_H^{\text{D-J}}\begin{bmatrix}s_{a,z}\\ s_{b,z}\\ s^{\text{D-J}}_{\text{ZQ},y}\\ s^{\text{D-J}}_{\text{ZQ},x}\end{bmatrix}(t)=\begin{bmatrix}0&0&-DJ_{ab}(t)/2&0\\ 0&0&DJ_{ab}(t)/2&0\\ DJ_{ab}(t)&-DJ_{ab}(t)&0&-\Delta\omega_{ab}(t)\\ 0&0&\Delta\omega_{ab}(t)&0\end{bmatrix}\begin{bmatrix}s_{a,z}\\ s_{b,z}\\ s^{\text{D-J}}_{\text{ZQ},y}\\ s^{\text{D-J}}_{\text{ZQ},x}\end{bmatrix}(t) \tag{13}$$

In many circumstances the dipolar interaction is relatively large and therefore it will be necessary to use this Bloch type of Liouvillian. Of course, in the case of large coupling we have to realize that the "single event at the time" assumption could be violated, i.e there may be an overlap between a μw and a D-J rotor-event. Assuming independent rotor-event, the three spin system evolution can be obtained by combining operators $\widehat{\widehat{L}}_H^{\mu\text{w}}$ and $\widehat{\widehat{L}}_H^{\text{D-J}}$ in equations 11 and 13. This results in a 8×8 Liouville operator, after the addition of $\{s^{\text{D-J}}_{\text{ZQ},x},s^{\text{D-J}}_{\text{ZQ},y}\}$ to the six terms of $\sigma_{\mu\text{w}}$. Once relaxation is added, that leads to a 9×9, $\widehat{\widehat{L}}_B^{\mu\text{w}\oplus\text{D-J}}$ matrix that is much smaller than the 16×16 problem size required in the full Liouville space calculations.

When the dipolar interaction is weak and the duration of the D-J rotor-event is short enough such that the transverse relaxation can be ignored, we can use the L-Z formula for the change of the single $s_{\text{ZQ},z}(t)$ element only. However the fact that our presentation for describing the μw events involves already $s_{a,z}(t)$ and $s_{b,z}(t)$, we first

write the L-Z propagator $\widehat{\widehat{U}}_{\mathrm{LZ},\kappa}$ of the κ^{th} time interval as :

$$\begin{bmatrix} s_{\mathrm{DQ},z} \\ s_{\mathrm{ZQ},z} \end{bmatrix}(t_{\kappa-1}^{+}) = \widehat{\widehat{U}}_{\mathrm{LZ},\kappa} \begin{bmatrix} s_{\mathrm{DQ},z} \\ s_{\mathrm{ZQ},z} \end{bmatrix}(t_{k-1}) = \begin{bmatrix} 1 & 0 \\ 0 & 1-2\epsilon_{\mathrm{D/J}} \end{bmatrix} \begin{bmatrix} s_{\mathrm{DQ},z} \\ s_{\mathrm{ZQ},z} \end{bmatrix}(t_{k-1})$$

with

$$\epsilon_{\mathrm{D/J}} = 1 - \exp\left[\frac{-\pi|D_{ab}+2J_{ab}|^2_{t_{\kappa-1}}}{2\left(\frac{\mathrm{d}\Delta\omega_{ab}}{\mathrm{d}t}\right)}\right] \text{ if D} - \text{J crossing, or } = 0 \text{ if no crossing}$$

and then use the transformation of Eq. 12 to combine the LZ approach of the μw and the D-J events. The obtained dimension of the Liouville space stays 3×3 and the D-J event taking single quantum T_1 relaxation into account

$$\begin{aligned}\begin{bmatrix} 1 \\ s_{a,z} \\ s_{b,z} \end{bmatrix}(t_\kappa) &= \exp(\widehat{\widehat{R}}_1\delta t)\widehat{\widehat{U}}^{\mathrm{D/J}}_{\mathrm{LZ},\kappa} \begin{bmatrix} 1 \\ s_{a,z} \\ s_{b,z} \end{bmatrix}(t_{\kappa-1}) \\ &= \begin{bmatrix} 0 & 0 & 0 \\ [s^{eq}_{a,z}(1-e^{-\delta t/T_1})] & [1-\epsilon_{\mathrm{D/J}}+e^{-\delta t/T_1}] & \epsilon_{\mathrm{D/J}} \\ [s^{eq}_{b,z}(1-e^{-\delta t/T_1})] & \epsilon_{\mathrm{D/J}} & [1-\epsilon_{\mathrm{D/J}}+e^{-\delta t/T_1}] \end{bmatrix} \begin{bmatrix} 1 \\ s_{a,z} \\ s_{b,z} \end{bmatrix}(t_{\kappa-1})\end{aligned}$$

The above calculations account for the presence of an electron exchange interaction $J_{a,b}$ (see equation 2) that are smaller than the EPR linewidth otherwise, the basis isn't appropriate to describe the events. The product state representation of the spin states during crossing and in between must be modified, which complicates our discussion.

3. The CE rotor-events

In a similar fashion as the first two rotor-events, the cross-effect rotor-events have their own frequency matching conditions. When the nuclear Larmor frequency ω_n is much larger than the value of $D-J_{ab}$, two conditions are met when $|\omega_a(t_k)-\omega_b(t_k)| \simeq \pm\omega_n$ (more rigorous expressions can be found in [1, 6–9]). These two types of CE events occur when the energies of $|\alpha_a\beta_b\alpha_n\rangle$ and $|\beta_a\alpha_b\beta_n\rangle$ (CE$^-$: $\omega_a(t)-\omega_b(t) \simeq -\omega_n$) or when $|\beta_a\alpha_b\alpha_n\rangle$ and $|\alpha_a\beta_b\beta_n\rangle$ (CE$^+$:$\omega_a(t)-\omega_b(t) \simeq +\omega_n$) match. To simplify the forthcoming discussion we define the eight spin states of the three-spin system as follows:

$$\begin{aligned} |1\rangle = |\alpha_a\alpha_b\beta_n\rangle \quad ; \quad |2\rangle = |\alpha_a\alpha_b\alpha_n\rangle \quad ; \quad |3\rangle = |\alpha_a\beta_b\beta_n\rangle \quad ; \quad |4\rangle = |\alpha_a\beta_b\alpha_n\rangle \\ |5\rangle = |\beta_a\alpha_b\beta_n\rangle \quad ; \quad |6\rangle = |\beta_a\alpha_b\alpha_n\rangle \quad ; \quad |7\rangle = |\beta_a\beta_b\beta_n\rangle \quad ; \quad |8\rangle = |\beta_a\beta_b\alpha_n\rangle \end{aligned}$$

In this notation the $|1\rangle-|7\rangle$ and $|2\rangle-|8\rangle$ transitions are electron DQ transitions and the $|3\rangle-|5\rangle$ and $|4\rangle-|6\rangle$ are the electron ZQ transitions. The even states are nuclear $|\chi_a\phi_b\alpha_n\rangle$ states and the odd ones $|\chi_a\phi_b\beta_n\rangle$ states. The CE events happen when the four states $|3\rangle$ to $|6\rangle$ meet each other. Thus the CE$^-$and CE$^+$events involve

$$CE^- : \quad |4\rangle \leftrightarrow |5\rangle \quad ; \quad CE^+ : \quad |3\rangle \leftrightarrow |6\rangle.$$

The computational approach for finding the necessary $s^{(m)}(t)$ elements that compose the $\sigma(t)$ vector describing the CE events is more complex than in the case of the events discussed earlier. The Hamiltonian defining the spin system does not contain matrix elements between the crossing states and therefore it is not straightforward to determine directly the coefficients of the fictitious spin-half operators $\widehat{S}_x^{\text{CE-}}, \widehat{S}_y^{\text{CE-}}, \widehat{S}_z^{\text{CE-}}$ of the transition $|4\rangle-|5\rangle$ and $\widehat{S}_x^{\text{CE+}}, \widehat{S}_y^{\text{CE+}}, \widehat{S}_z^{\text{CE+}}$ of $|3\rangle-|6\rangle$. As previously shown by Hu and others [6–8], effective matrix elements between two CE crossing states can be derived using degenerate perturbation theory when the spin-spin interactions are smaller than the nuclear Zeeman interaction (high field approximation). The presence of the flip-flop dipolar coupling matrix elements connecting the ZQ states $\langle 4|\widehat{H}_{\mathrm{D-J}}|6\rangle$ (and $\langle 3|\widehat{H}_{\mathrm{D-J}}|5\rangle$), and the existence of pseudo-secular hyperfine coupling matrix element of the nuclear transitions $\langle 6|\widehat{H}_{\mathrm{HF}}|5\rangle$ (and $\langle 3|\widehat{H}_{\mathrm{HF}}|4\rangle$), combined with the ω_n energy difference connects the levels $|4\rangle-|5\rangle$ and $|6\rangle$ (and $|3\rangle-|6\rangle$ and $|5\rangle$) via an effective matrix element $\langle 4|\widehat{H}_{\mathrm{CE-}}|5\rangle$ (and $\langle 3|\widehat{H}_{\mathrm{CE+}}|6\rangle$). These effective elements can then be used to introduce the fictitious spin-half

operator, assuming it is real, into the Hamiltonian operator expansion with the coefficient [7]

$$h_x^{\mathrm{CE}}\widehat{S}_x^{\mathrm{CE}\pm} = \sqrt{(A^+)^2 + (A^-)^2}D_{a,b}/\omega_n\widehat{S}_x^{\mathrm{CE}\pm}$$

with

$$\langle 4|\widehat{S}_x^{\mathrm{CE}-}|5\rangle = 1/2 \quad ; \quad \langle 3|\widehat{S}_x^{\mathrm{CE}+}|6\rangle = 1/2$$

At this point we should try to express the Hamiltonian using the $\widehat{S}_p^{\mathrm{CE}\pm}$ operators. Since these operators only have matrix elements in the electron ZQ subspace defined by the states $\{|3\rangle, |4\rangle, |5\rangle, |6\rangle\}$ we split the Hamiltonian in two terms, $\widehat{H}_{\mathrm{CE}}(t)$ that contains operators in the ZQ subspace and $\widehat{H}_{\mathrm{non-CE}}(t)$ which does not influence the CE rotor-events

$$\widehat{H}(t) = \widehat{H}_{\mathrm{CE}}(t) + \widehat{H}_{\mathrm{non-CE}}(t).$$

This is made possible by projecting the $\widehat{I}_{n,z}$ operator in two parts $\widehat{I}_{n,z} = \widehat{I}_{n,z}^{\mathrm{ZQ}} + \widehat{I}_{n,z}^{\mathrm{DQ}}$ as well. The first $\widehat{I}_{n,z}^{\mathrm{ZQ}}$ has four matrix elements in the ZQ subspace $\{|3\rangle, |4\rangle, |5\rangle, |6\rangle\}$ and $\widehat{I}_{n,z}^{\mathrm{DQ}}$ has four elements in the electron DQ subspace $\{|1\rangle, |2\rangle, |7\rangle, |8\rangle\}$. After replacing the dipolar flip-flop operator term $(\widehat{S}_a^+\widehat{S}_b^- + \widehat{S}_a^-\widehat{S}_b^+)$, and the pseudo-secular hyperfine operator terms $(\widehat{S}_{a,z}\widehat{I}_{n,p})$ with $p = x, y$, by the $h_x^{\mathrm{CE}}\widehat{S}_x^{\mathrm{CE}\pm}$ terms we get that

$$\widehat{H}_{\mathrm{CE}}(t) = 1/2(\omega_a(t) - \omega_b(t))(\widehat{S}_{a,z} - \widehat{S}_{b,z}) + \omega_n\widehat{I}_{n,z}^{\mathrm{ZQ}} + h_x^{\mathrm{CE}}\widehat{S}_x{}^{\mathrm{CE}+} + h_x^{\mathrm{CE}}\widehat{S}_x{}^{\mathrm{CE}\text{-}}$$
$$\widehat{H}_{\mathrm{non-CE}}(t) = 1/2(\omega_a(t) + \omega_b(t))(\widehat{S}_{a,z} + \widehat{S}_{b,z}) + \omega_n\widehat{I}_{n,z}^{\mathrm{DQ}} + A\widehat{S}_{a,z}\widehat{I}_{n,z} + D\widehat{S}_{a,z}\widehat{S}_{b,z}$$

The last two terms in $\widehat{H}_{\mathrm{non-CE}}(t)$, although with matrix elements in the ZQ subspace, do not influence the CE event spin dynamics. The $\widehat{H}_{\mathrm{CE}}$ part of the Hamiltonian can be rewritten:

$$\widehat{H}_{\mathrm{CE}}(t) = \Delta\omega^{\mathrm{CE}\text{-}}\widehat{S}_z{}^{\mathrm{CE}\text{-}} + \Delta\omega^{\mathrm{CE}+}\widehat{S}_z{}^{\mathrm{CE}+} + h_x^{\mathrm{CE}}\widehat{S}_x{}^{\mathrm{CE}+} + h_x^{\mathrm{CE}}\widehat{S}_x{}^{\mathrm{CE}\text{-}}$$

using the following notations

$$\Delta\omega^{\mathrm{CE}\text{-}} = (\omega_a(t) - \omega_b(t) + \omega_n)$$
$$\Delta\omega^{\mathrm{CE}+} = (\omega_a(t) - \omega_b(t) - \omega_n)$$

and

$$\widehat{S}_z{}^{\mathrm{CE}\text{-}} = {}^1\!/_2((\widehat{S}_{a,z} - \widehat{S}_{b,z})/2 + \widehat{I}_{n,z}^{\mathrm{ZQ}})$$
$$\widehat{S}_z{}^{\mathrm{CE}+} = {}^1\!/_2((\widehat{S}_{a,z} - \widehat{S}_{b,z})/2 - \widehat{I}_{n,z}^{\mathrm{ZQ}})$$

We can then derive a 6×6 Liouvillian operating on a $\sigma(t)$ vector consisting of the coefficients $\{s_z{}^{\mathrm{CE}+}, s_z{}^{\mathrm{CE}\text{-}}, s_y{}^{\mathrm{CE}+}, s_x{}^{\mathrm{CE}+}, s_y{}^{\mathrm{CE}\text{-}}, s_x$
However, to combine these coefficients with the $\sigma_{\mu\mathrm{w}}(t)+\sigma_{\mathrm{D/J}}(t)$ vector we must add two coefficients of two additional operators with the same norm as $\widehat{S}_z{}^{\mathrm{CE}+}$ and $\widehat{S}_z^{\mathrm{CE}\text{-}}$, namely the DQ space operators $\widehat{S}_{ab,z}^{DQ} = (2^{-3/2})(\widehat{S}_{a,z} + \widehat{S}_{b,z})$ and $S_{n,z}^{\mathrm{DQ}} = (2^{-1/2})\widehat{I}_{n,z}^{\mathrm{DQ}}$, with $s_{ab,z}^{\mathrm{DQ}}$ and $s_{n,z}^{\mathrm{DQ}}$ respectively. σ_{CE} becomes $\{s_z{}^{\mathrm{CE}+}, s_z{}^{\mathrm{CE}\text{-}}, s_{ab,z}^{\mathrm{DQ}}, s_{n,z}^{\mathrm{DQ}}, s_y{}^{\mathrm{CE}+}, s_x{}^{\mathrm{CE}+}, s_y{}^{\mathrm{CE}\text{-}}, s_x{}^{\mathrm{CE}\text{-}}\}$.
We can now derive the form of the Liouville operator $\widehat{\widehat{L}}_H^{\mathrm{CE}}(t) = \widehat{\widehat{L}}_H^{\mathrm{CE}+}(t) + \widehat{\widehat{L}}_H^{\mathrm{CE}-}(t)$ starting with (the time dependence is omitted here for formatting reasons)

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} s_z{}^{\mathrm{CE}+} \\ s_z{}^{\mathrm{CE}\text{-}} \\ s_{ab,z}^{\mathrm{DQ}} \\ s_{n,z}^{\mathrm{DQ}} \\ s_y{}^{\mathrm{CE}+} \\ s_x{}^{\mathrm{CE}+} \\ s_y{}^{\mathrm{CE}\text{-}} \\ s_x{}^{\mathrm{CE}\text{-}} \end{bmatrix} = \widehat{\widehat{L}}_{\mathrm{CE}}^{H} \begin{bmatrix} s_z{}^{\mathrm{CE}+} \\ s_z{}^{\mathrm{CE}\text{-}} \\ s_{ab,z}^{\mathrm{DQ}} \\ s_{n,z}^{\mathrm{DQ}} \\ s_y{}^{\mathrm{CE}+} \\ s_x{}^{\mathrm{CE}+} \\ s_y{}^{\mathrm{CE}\text{-}} \\ s_x{}^{\mathrm{CE}\text{-}} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & h_x^{\mathrm{CE}+} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & h_x{}^{\mathrm{CE}\text{-}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -h_x^{\mathrm{CE}+} & 0 & 0 & 0 & 0 & -\Delta\omega^{\mathrm{CE}+} & 0 & 0 \\ 0 & 0 & 0 & 0 & \Delta\omega^{\mathrm{CE}+} & 0 & 0 & 0 \\ 0 & -h_x{}^{\mathrm{CE}\text{-}} & 0 & 0 & 0 & 0 & 0 & -\Delta\omega^{\mathrm{CE}\text{-}} \\ 0 & 0 & 0 & 0 & 0 & 0 & \Delta\omega^{\mathrm{CE}\text{-}} & 0 \end{bmatrix} \begin{bmatrix} s_z{}^{\mathrm{CE}+} \\ s_z{}^{\mathrm{CE}\text{-}} \\ s_{ab,z}^{\mathrm{DQ}} \\ s_{n,z}^{\mathrm{DQ}} \\ s_y{}^{\mathrm{CE}+} \\ s_x{}^{\mathrm{CE}+} \\ s_y{}^{\mathrm{CE}\text{-}} \\ s_x{}^{\mathrm{CE}\text{-}} \end{bmatrix} \tag{14}$$

When we want to combine this vector with the $\sigma_{\mu w}(t) + \sigma_{D/J}(t)$ vector we have to perform the following transformation in order to reach the elements $\{s_{a,z}, s_{b,z}, s_{n,z}, s_z^{res}, s_y{}^{\text{CE+}}, s_x{}^{\text{CE+}}, s_y{}^{\text{CE-}}, s_x{}^{\text{CE-}}\}$:

$$\frac{1}{2}\begin{bmatrix} s_{a,z} \\ s_{b,z} \\ s_{n,z} \\ s_z^{\text{res}} \\ s_y{}^{\text{CE+}} \\ s_x{}^{\text{CE+}} \\ s_y{}^{\text{CE-}} \\ s_x{}^{\text{CE-}} \end{bmatrix} = \frac{1}{4}\begin{bmatrix} 1 & 1 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ -1 & -1 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 \\ -1 & 1 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} s_z{}^{\text{CE+}} \\ s_z{}^{\text{CE-}} \\ s_{ab,z}^{\text{DQ}} \\ s_{n,z}^{\text{DQ}} \\ s_y{}^{\text{CE+}} \\ s_x{}^{\text{CE+}} \\ s_y{}^{\text{CE-}} \\ s_x{}^{\text{CE-}} \end{bmatrix},$$

where we have added the operator $\widehat{S}_z^{\text{res}} = \widehat{I}_z^{\text{DQ}} - \widehat{I}_z^{\text{ZQ}} = 4\widehat{I}_z\widehat{S}_{a,z}\widehat{S}_{b,z}$ to maintain the dimensionality of the vector after the transformation. After the transformation of Eq. 14 becomes (the time dependence is omitted here for formatting reasons)

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} s_{a,z} \\ s_{b,z} \\ s_{n,z} \\ s_z^{res} \\ s_y{}^{\text{CE+}} \\ s_x{}^{\text{CE+}} \\ s_y{}^{\text{CE-}} \\ s_x{}^{\text{CE-}} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & \frac{1}{4}h_x^{\text{CE+}} & 0 & \frac{1}{4}h_x{}^{\text{CE-}} & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{4}h_x^{\text{CE+}} & 0 & -\frac{1}{4}h_x{}^{\text{CE-}} & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{4}h_x^{\text{CE+}} & 0 & \frac{1}{4}h_x{}^{\text{CE-}} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{4}h_x^{\text{CE+}} & 0 & -\frac{1}{4}h_x{}^{\text{CE-}} & 0 \\ -h_x^{\text{CE+}} & -h_x^{\text{CE+}} & h_x^{\text{CE+}} & -h_x^{\text{CE+}} & 0 & -\Delta\omega^{\text{CE+}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \Delta\omega^{\text{CE+}} & 0 & 0 & 0 \\ -h_x{}^{\text{CE-}} & h_x{}^{\text{CE-}} & -h_x{}^{\text{CE-}} & h_x{}^{\text{CE-}} & 0 & 0 & 0 & -\Delta\omega^{\text{CE-}} \\ 0 & 0 & 0 & 0 & 0 & 0 & \Delta\omega^{\text{CE-}} & 0 \end{bmatrix} \begin{bmatrix} s_{a,z} \\ s_{b,z} \\ s_{n,z} \\ s_z^{res} \\ s_y{}^{\text{CE+}} \\ s_x{}^{\text{CE+}} \\ s_y{}^{\text{CE-}} \\ s_x{}^{\text{CE-}} \end{bmatrix}$$

Joining the elements of σ_{CE} with the elements of $\sigma_{\mu w} + \sigma_{D/J}$ we have to add the $\{s_z^{res}, s_p^{\text{CE}\pm}, p = x, y\}$ coefficients to the last vector. In practice it turns out that the value $s_z^{res}(t)$, which is the coefficient of the tri-linear $\widehat{S}_z^{\text{res}} = 4\widehat{I}_z\widehat{S}_{a,z}\widehat{S}_{b,z}$ operator that is initially equal to zero, does not contribute to the time dependence of the other coefficients and it can be ignored during the calculations. This was shown in equation 36-37 in ref [10]. The operators involved in this derivation can all be expressed in terms of the z-components of the electron and nuclear angular momentum operators:

$$\begin{aligned}
\widehat{S}_z{}^{\text{CE+}} &= \frac{1}{2}(\widehat{S}_z^{\text{ZQ}} + 4\widehat{S}_z^{\text{ZQ}}) = \frac{1}{4}(\widehat{S}_{a,z} - \widehat{S}_{b,z})(1 + 2\widehat{I}_{n,z}) \\
\widehat{S}_z{}^{\text{CE-}} &= \frac{1}{2}(\widehat{S}_z^{\text{ZQ}} - 4\widehat{S}_z^{\text{ZQ}}) = \frac{1}{4}(\widehat{S}_{a,z} - \widehat{S}_{b,z})(1 - 2\widehat{I}_{n,z}) \\
\widehat{S}_z^{\text{DQ}} &= \frac{1}{2\sqrt{2}}(\widehat{S}_{a,z} + \widehat{S}_{b,z}) \\
\widehat{S}_{n,z}^{\text{DQ}} &= \frac{1}{\sqrt{2}}\widehat{I}_{n,z}^{\text{DQ}} = \frac{1}{2\sqrt{2}}\widehat{I}_{n,z}(1 + 4\widehat{S}_{a,z}\widehat{S}_{b,z}) \\
\widehat{S}_z^{\text{res}} &= \widehat{I}_z^{\text{DQ}} - \widehat{I}_z^{\text{ZQ}} = 4\widehat{I}_{n,z}\widehat{S}_{a,z}\widehat{S}_{b,z}
\end{aligned}$$

In general, CE rotor-events are usually fast and it is usually possible to assess the amount of polarization, that is transferred between the spins using the LZ approximation. If the off-diagonal element lead to a crossing of efficiency:

$$\epsilon_{\text{CE}\pm} = \left[2\exp\left[\frac{-\pi|h_x^{\text{CE}}|^2}{2\left(\frac{\mathrm{d}\omega_{\text{CE}}^{\pm}}{\mathrm{d}t}\right)}\right] - 1\right]$$

then the LZ approach can be applied to describe the CE events using the $\widehat{S}_z{}^{\text{CE+}}(t)$ and $\widehat{S}_z{}^{\text{CE-}}(t)$ coefficients. Adding the $s_{ab,z}^{\text{DQ}}$ and $s_{n,z}^{\text{DQ}}$ elements the crossing can be represented as:

$$\begin{bmatrix} s_z^{\text{CE+}} \\ s_z^{\text{CE-}} \\ s_{ab,z}^{\text{DQ}} \\ s_{n,z}^{\text{DQ}} \end{bmatrix}(t_{k-1}^{+}) = \begin{bmatrix} \epsilon_{\text{CE-}} & 0 & 0 & 0 \\ 0 & \epsilon_{\text{CE-}} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} s_z^{\text{CE+}} \\ s_z^{\text{CE-}} \\ s_{ab,z}^{\text{DQ}} \\ s_{n,z}^{\text{DQ}} \end{bmatrix}(t_{k-1})$$

using the above transformations, and ignoring the s_z^{res} coefficient, we obtain:

$$\begin{bmatrix} s_{a,z} \\ s_{b,z} \\ s_{n,z} \end{bmatrix}(t_{k+1}) = \hat{\hat{L}}_{\rm CE}^{\rm LZ} \begin{bmatrix} s_{a,z} \\ s_{b,z} \\ s_{n,z} \end{bmatrix}(t_{k-1}) = \frac{1}{4}\begin{bmatrix} 3+\epsilon_{\rm CE\pm} & 1-\epsilon_{\rm CE\pm} & \pm(1-\epsilon_{\rm CE\pm}) \\ 1-\epsilon_{\rm CE\pm} & 3+\epsilon_{\rm CE\pm} & \mp(1-\epsilon_{\rm CE\pm}) \\ \pm(1-\epsilon_{\rm CE\pm}) & \mp(1-\epsilon_{\rm CE\pm}) & 3+\epsilon_{\rm CE\pm} \end{bmatrix}\begin{bmatrix} s_{a,z}(t_{k-1}) \\ s_{b,z}(t_{k-1}) \\ s_{n,z}(t_{k-1}) \end{bmatrix}$$

The combine $(\hat{\hat{L}}_{LZ}^{\mu\rm w} + \hat{\hat{L}}_{LZ}^{\rm D\text{-}J} + \hat{\hat{L}}_{LZ}^{\rm CE+} + \hat{\hat{L}}_{LZ}^{\rm CE-})$ is at this point in the discussion is of a dimension (3×3), the number of spins in the system.

4. *The SE rotor-events*

The SE rotor-events occur when the μw irradiation is "on resonance" with, for instance, the electron a - nucleus zero quantum transition $|\alpha_a\chi_b\beta_n\rangle \leftrightarrow |\beta_a\chi_b\alpha_n\rangle$or double quantum transition $|\alpha\chi\alpha\rangle \leftrightarrow |\beta\chi\alpha\rangle$ which correspond to the matching conditions $(\omega_a - \omega_{\mu\rm w} \simeq \omega_n)$ or $(\omega_a - \omega_{\mu\rm w} \simeq -\omega_n)$ respectively. The hyperfine interaction between electron a and the nucleus n can be represented by the secular and the pseudo-secular terms in the Hamiltonian, which are assumed to be much smaller than the nuclear Zeeman interaction (high field approximation). The application of perturbation theory allows diagonalizing the Hamiltonian, shifting the energy levels by an amount of the order of $\eta_{HF} = \{A^+(t)^2 + A^-(t)^2/\omega_n^2\}$. As shown previously, for instance by Corzilius et al. [11], such an effect can be accounted for by replacing the the $\widehat{S}_x$ operator of the μw Hamiltonian by:

$$\widehat{S}_x \rightarrow \widehat{S}_x + (1/2)\eta_{HF}\{(\widehat{S}_a^+\widehat{I}_n^- + \widehat{S}_a^-\widehat{I}_n^+) + (\widehat{S}_a^+\widehat{I}_n^+ + \widehat{S}_a^-\widehat{I}_n^-)\}.$$

The two additional terms become significant in the rotating frame Hamiltonian when the μw frequency is close to the ZQ and DQ transition frequencies. Ignoring for simplicity the energy shifts induced by the hyperfine interactions, we can write the following effective Hamiltonians:

$$\widehat{H}_{\rm ZQ} = (1/2)\Delta\omega_{\rm ZQ}^{\rm SE}(\widehat{S}_{a,z} - \widehat{I}_{n,z}) + (1/2)\omega_1^{\rm SE}(\widehat{S}_a^+\widehat{I}_n^- + \widehat{S}_a^-\widehat{I}_n^+) \quad ; \quad \Delta\omega_{\rm ZQ}^{\rm SE} = (\omega_a(t) + \omega_{\mu w} - \omega_n) \quad , \quad \omega_1^{\rm SE} = \eta_{HF}\omega_1$$
$$\widehat{H}_{\rm DQ} = (1/2)\Delta\omega_{\rm DQ}^{\rm SE}(\widehat{S}_{a,z} + I_{n,z}) + (1/2)\omega_1^{SE}(S_a^+I_n^+ + S_a^-I_n^-) \quad ; \quad \Delta\omega_{\rm DQ}^{\rm SE} = (\omega_a(t) + \omega_{\mu w} - \omega_n) \quad , \quad \omega_1^{\rm SE} = \eta_{HF}\omega_1$$

which represent the two ZQ- and DQ-SE events with $\chi_b = \alpha_b, \beta_b$. The Liouville operators corresponding to these Hamiltonians must be represented in the appropriate $s^{(m)}$ representations. Similarly to the CE events, we can choose the two representations $\{s_x^{\rm ZQ}, s_y^{\rm ZQ}, s_z^{\rm ZQ}\}$ and $\{s_x^{\rm DQ}, s_y^{\rm DQ}, s_z^{\rm DQ}\}$, where these coefficients corresponding to the following operators in the density matrix expansion are:

$$\widehat{S}_x^{{\rm ZQ}a} = (1/2)(\widehat{S}_a^+\widehat{I}_n^- + \widehat{S}_a^-\widehat{I}_n^+) \quad ; \quad \widehat{S}_y^{{\rm ZQ}a} = (i/2)(\widehat{S}_a^+\widehat{I}_n^- - \widehat{S}_a^-\widehat{I}_n^+)$$
$$\widehat{S}_x^{{\rm DQ}a} = (1/2)(\widehat{S}_a^+\widehat{I}_n^+ + \widehat{S}_a^-\widehat{I}_n^-) \quad ; \quad \widehat{S}_y^{{\rm DQ}a} = (i/2)(\widehat{S}_a^+\widehat{I}_n^+ - \widehat{S}_a^-\widehat{I}_n^-)$$
$$\widehat{S}_z^{{\rm ZQ}a} = (1/2)(\widehat{S}_{a,z} - \widehat{I}_{n,z}) \quad ; \quad \widehat{S}_z^{{\rm DQ}a} = (1/2)(\widehat{S}_{a,z} + \widehat{I}_{n,z})$$

The Liouville operators take the form

$$\frac{\rm d}{{\rm d}t}\begin{bmatrix} s_z^{{\rm ZQ}a} \\ s_y^{{\rm ZQ}a} \\ s_x^{{\rm ZQ}a} \\ s_z^{{\rm DQ}a} \end{bmatrix} = \hat{\hat{L}}_{\rm SE}^{{\rm ZQ}a}(t)\begin{bmatrix} s_z^{{\rm ZQ}a} \\ s_y^{{\rm ZQ}a} \\ s_x^{{\rm ZQ}a} \\ s_z^{{\rm DQ}a} \end{bmatrix} = \begin{bmatrix} 0 & -\omega_1^{\rm SE}(t) & 0 & 0 \\ -\omega_1^{\rm SE}(t) & 0 & -\Delta\omega_{\rm ZQ}(t) & 0 \\ 0 & \Delta\omega_{\rm ZQ}(t) & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} s_z^{{\rm ZQ}a} \\ s_y^{{\rm ZQ}a} \\ s_x^{{\rm ZQ}a} \\ s_z^{{\rm DQ}a} \end{bmatrix}$$

$$\frac{\rm d}{{\rm d}t}\begin{bmatrix} s_z^{{\rm DQ}a} \\ s_y^{{\rm DQ}a} \\ s_x^{{\rm DQ}a} \\ s_z^{{\rm ZQ}a} \end{bmatrix} = \hat{\hat{L}}_{\rm SE}^{{\rm DQ}a}(t)\begin{bmatrix} s_z^{{\rm DQ}a} \\ s_y^{{\rm DQ}a} \\ s_x^{{\rm DQ}a} \\ s_z^{{\rm ZQ}a} \end{bmatrix} = \begin{bmatrix} 0 & -\omega_1^{\rm SE}(t) & 0 & 0 \\ -\omega_1^{\rm SE}(t) & 0 & -\Delta\omega_{\rm DQ}(t) & 0 \\ 0 & \Delta\omega_{\rm DQ}(t) & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} s_z^{{\rm DQ}a} \\ s_y^{{\rm DQ}a} \\ s_x^{{\rm DQ}a} \\ s_z^{{\rm ZQ}a} \end{bmatrix}$$

These equations can be transformed to the basis $\{s_{a,z}, s_{n,z}, s_y^{\mathrm{ZQ}a}, s_x^{\mathrm{ZQ}a}, s_y^{\mathrm{DQ}a}, s_x^{\mathrm{DQ}a}\}$ via the definitions of $\widehat{S}_z^{\mathrm{ZQ/DQ}a}$

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} s_{a,z} \\ s_{n,z} \\ s_y^{\mathrm{ZQ}a} \\ s_x^{\mathrm{ZQ}a} \\ s_y^{\mathrm{DQ}a} \\ s_x^{\mathrm{DQ}a} \end{bmatrix} = \widehat{\widehat{L}}_H^{\mathrm{SE}}(t) \begin{bmatrix} s_{a,z} \\ s_{n,z} \\ s_y^{\mathrm{ZQ}a} \\ s_x^{\mathrm{ZQ}a} \\ s_y^{\mathrm{DQ}a} \\ s_x^{\mathrm{DQ}a} \end{bmatrix} = \begin{bmatrix} 0 & 0 & \omega_1^{\mathrm{SE}}(t) & 0 & \omega_1^{\mathrm{SE}}(t) & 0 \\ 0 & 0 & -\omega_1^{\mathrm{SE}}(t) & 0 & \omega_1^{\mathrm{SE}}(t) & 0 \\ -\omega_1^{\mathrm{SE}}(t)/2 & \omega_1^{\mathrm{SE}}(t)/2 & 0 & -\Delta\omega_{\mathrm{ZQ}}(t) & 0 & 0 \\ 0 & 0 & \Delta\omega_{\mathrm{ZQ}}(t) & 0 & 0 & 0 \\ -\omega_1^{\mathrm{SE}}(t)/2 & -\omega_1^{\mathrm{SE}}(t)/2 & 0 & 0 & 0 & -\Delta\omega_{\mathrm{DQ}}(t) \\ 0 & 0 & 0 & 0 & \Delta\omega_{\mathrm{DQ}}(t) & 0 \end{bmatrix} \begin{bmatrix} s_{a,z} \\ s_{n,z} \\ s_y^{\mathrm{ZQ}a} \\ s_x^{\mathrm{ZQ}a} \\ s_y^{\mathrm{DQ}a} \\ s_x^{\mathrm{DQ}a} \end{bmatrix}$$

To include the SE to the previous description, we need to complement the manifold of 14 coefficients of ($\widehat{\widehat{L}}_B^{\mu\mathrm{w}} + \widehat{\widehat{L}}_B^{\mathrm{D\text{-}J}} + \widehat{\widehat{L}}_B^{\mathrm{CE}}$) with $\{s_x^{\mathrm{ZQ}a}, s_y^{\mathrm{ZQ}a}, s_x^{\mathrm{DQ}a}, s_y^{\mathrm{DQ}a}\}$ to reach the final 18×18 Liouville operator ($\widehat{\widehat{L}}_B^{\mu\mathrm{w}} + \widehat{\widehat{L}}_B^{\mathrm{D\text{-}J}} + \widehat{\widehat{L}}_B^{\mathrm{CE}} + \widehat{\widehat{L}}_B^{\mathrm{SE}}$).

In general the SE events are relatively short in duration, and thus can be represented by the Landau-Zener approach. We obtain:

$$\begin{bmatrix} s_z^{\mathrm{ZQ}a} \\ s_z^{\mathrm{DQ}a} \end{bmatrix}(t_{k-1}) = \begin{bmatrix} \epsilon_{SE}^{\mathrm{ZQ}} & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} s_z^{\mathrm{ZQ}a} \\ s_z^{\mathrm{DQ}a} \end{bmatrix}(t_{k+1}) \quad ; \quad \begin{bmatrix} s_z^{\mathrm{ZQ}a} \\ s_z^{\mathrm{DQ}a} \end{bmatrix}(t_{k-1}) = \begin{bmatrix} 1 & 0 \\ 0 & \epsilon_{SE}^{\mathrm{DQ}a} \end{bmatrix} \begin{pmatrix} s_z^{\mathrm{ZQ}a} \\ s_z^{\mathrm{DQ}a} \end{pmatrix}(t_{k+1})$$

with

$$\epsilon_{\mathrm{SE}} = \left[2\exp\left[\frac{-\pi|\omega_1^{\mathrm{eff}}|^2}{2\left(\frac{\mathrm{d}\omega_{\mathrm{DQ/ZQ}}}{\mathrm{d}t}\right)} \right] - 1 \right]$$

If we know perform a basis change ,we can rewrite the effect of the propagator $\widehat{\widehat{U}}_{\mathrm{SE}}^{\mathrm{LZ}}$ in the basis $\{s_z^a, s_z^b\}$:

$$\begin{bmatrix} s_{a,z} \\ s_{n,z} \end{bmatrix}(t_{k+1}) = \widehat{\widehat{U}}_{\mathrm{LZ},\kappa}^{\mathrm{SE}} \begin{bmatrix} s_{a,z} \\ s_{n,z} \end{bmatrix}(t_k)$$

with

$$\widehat{\widehat{U}}_{\mathrm{LZ},\kappa}^{,\mathrm{SE}} = \begin{bmatrix} 1+\epsilon_{SE}^{\mathrm{ZQ}} & 1-\epsilon_{SE}^{\mathrm{ZQ}} \\ 1-\epsilon_{SE}^{\mathrm{ZQ}} & 1+\epsilon_{SE}^{\mathrm{ZQ}} \end{bmatrix} \qquad \text{or} \qquad \begin{bmatrix} 1+\epsilon_{SE}^{\mathrm{DQ}} & -1+\epsilon_{SE}^{\mathrm{DQ}} \\ -1+\epsilon_{SE}^{\mathrm{DQ}} & 1+\epsilon_{SE}^{\mathrm{DQ}} \end{bmatrix}$$

for ZQ-SE and DQ-SE rotor-events respectively.

5. Reduced "Bloch operator" and "LZ operator"

In order to compute MAS-DNP mechanisms, we need to derive Liouville operators but we also need to account for all relaxation pathways, namely the longitudinal and transverse relaxation times of the electrons T_1^e, T_2^e and the nucleus T_1^n, T_2^n. Previous work on MAS description of T_1 and the T_2 relaxation used in in DNP simulations [1, 10, 12] used definitions in the eigenbasis of the Hamiltonian. While this has little impact on the T_1 for high magnetic field and MAS simulations, it has more drastic effect on T_2. This is particularly critical for the D-J rotor-events as it impacts $T_{2,\mathrm{ZQ}}^e$'s definition. To be more specific let's consider two electrons with a frequency offset of the same magnitude as the D-J interaction. The eigenbasis of the 3 spin system is then $|\alpha\alpha\chi\rangle$, $a_1(t)|\alpha\beta\chi\rangle + a_2(t)|\beta\alpha\chi\rangle$, $a_2(t)|\alpha\beta\chi\rangle - a_1(t)|\beta\alpha\chi\rangle$ and $|\beta\beta\chi\rangle$, where $a_1(t)$ and $a_2(t)$ depends on the offset and the D-J interaction. χ stands for the nuclear state (either alpha or beta) and will be ignored in the following). During the dipolar rotor-event, the $T_{2,\mathrm{ZQ}}^e$ involves the loss of the coherence between the states $a_1(t)|\alpha\beta\rangle + a_2(t)|\beta\alpha\rangle$, $a_2(t)|\alpha\beta\rangle - a_1(t)|\beta\alpha\rangle$. In the eigenbasis $T_{2,\mathrm{ZQ}}^e$ depends therefore on the state mixing and becomes offset dependent: i.e. $1/T_{2,\mathrm{ZQ}}^e(t) \propto |a_1^2(t) - a_2^2(t)|$. Notably $1/T_{2,\mathrm{ZQ}}^e$ is equal to zero when the two electrons are on resonance and equal to $1/2T_2^e$ when offset term dominates. Nevertheless, the $T_{2,\mathrm{ZQ}}^e$ relaxation parameter was held constant in the present work, and simply approximate to $T_{2,\mathrm{ZQ}}^e = 2T_2^e$ since it gives correct results as compared to Full Liouville calculations. In the CE and SE rotor-event case, the treatment of relaxation appear to be even less critical. The state mixing only occurs for very short time periods contrary to the D-J rotor-events. To achieve complete analogy with the full Liouville calculations, we define $T_{2,\mathrm{CE}} = T_2^e/2 + T_2^n$ and $T_{2,\mathrm{SE}} = (T_2^e + T_2^n)/2$.

Assuming that the rotor-events are independent, the previous derivations can be combined into a single evolution

operator, sum of all individual operators.

$$\hat{\hat{L}}_B = \hat{\hat{L}}_B^{\mu\mathrm{w}} + \hat{\hat{L}}_B^{\text{D-J}} + \hat{\hat{L}}_B^{\mathrm{CE}} + \hat{\hat{L}}_B^{\mathrm{SE}}$$

In the end, the σ vector can be represented with the following coefficients $\{1, s_{a,z}, s_{a,y}, s_{a,x},\ s_{b,z}, s_{b,y}, s_{b,x}, s_{n,z}, s_{\mathrm{ZQ},y}, s_{\mathrm{ZQ},x},\ s_y^{\mathrm{CE}+}, s_x^{\mathrm{CE}+},\ s_y^{\mathrm{CE}-}, s_x^{\mathrm{CE}-}, s_y^{\mathrm{DQ}a}, s_x^{\mathrm{DQ}a}, s_y^{\mathrm{ZQ}a}, s_x^{\mathrm{ZQ}a}\}$ within the corresponding to the basis $\{\widehat{E},\ \widehat{S}_{a,z},\ \widehat{S}_{a,y},\ \widehat{S}_{a,x},\ \widehat{S}_{b,z},\ \widehat{S}_{b,y},\ \widehat{S}_{b,x},\ \widehat{S}_{\mathrm{ZQ},y},\ \widehat{S}_{\mathrm{ZQ,x}}\ \widehat{I}_{n,z},\ \widehat{S}_y^{\mathrm{CE}+},\ \widehat{S}_x^{\mathrm{CE}+},\ \widehat{S}_y^{\mathrm{CE}-},\ \widehat{S}_x^{\mathrm{CE}-}, \widehat{S}_y^{\mathrm{DQ}a},\ \widehat{S}_x^{\mathrm{DQ}a},\ \widehat{S}_y^{\mathrm{ZQ}a},\ \widehat{S}_x^{\mathrm{ZQ}a}\}$. This approach yields an homogeneous master equation, which allows computing efficiently the propagator of a periodic problem with significant time-savings. Finally the (restricted) Liouvillian becomes (time dependence of interactions is omitted):

$$\hat{\hat{L}}_B = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
s_{a,z}^{\mathrm{eq}}/T_{1,a}^e & -1/T_{1,a}^e & \omega_1 & 0 & 0 & 0 & 0 & D_{a,b} & 0 & 0 & h_x^{\mathrm{CE}+}/4 & 0 & h_x^{\mathrm{CE}-}/4 & 0 & \omega_1^{\mathrm{SE}} & 0 & \omega_1^{\mathrm{SE}} & 0 \\
0 & -\omega_1 & -1/T_2^e & -\Delta\omega_{\mathrm{a}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & -\Delta\omega_{\mathrm{a}} & -1/T_2^e & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
s_{b,z}^{\mathrm{eq}}/T_{1,b}^e & 0 & 0 & 0 & -1/T_{1,b}^e & \omega_1 & 0 & -D_{a,b} & 0 & 0 & -h_x^{\mathrm{CE}+}/4 & 0 & -h_x^{\mathrm{CE}-}/4 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -\omega_1 & -1/T_2^e & -\Delta\omega_{\mathrm{a}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -\Delta\omega_{\mathrm{a}} & -1/T_2^e & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -D_{a,b}/2 & 0 & 0 & D_{a,b}/2 & 0 & 0 & -2/T_{2,\mathrm{ZQ}}^e & -\Delta\omega_{\mathrm{D}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \Delta\omega_{\mathrm{D}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
s_{n,z}^{\mathrm{eq}}/T_1^n & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1/T_1^n & -h_x^{\mathrm{CE}+}/4 & 0 & h_x^{\mathrm{CE}-}/4 & 0 & \omega_1^{\mathrm{SE}} & 0 & -\omega_1^{\mathrm{SE}} & 0 \\
0 & -h_x^{\mathrm{CE}+} & 0 & 0 & h_x^{\mathrm{CE}+} & 0 & 0 & 0 & 0 & h_x^{\mathrm{CE}+} & -2/T_{2,\mathrm{CE}} & -\Delta\omega_{\mathrm{CE}}^+ & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \Delta\omega_{\mathrm{CE}}^+ & -2/T_{2,\mathrm{CE}} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -h_x^{\mathrm{CE}-} & 0 & 0 & h_x^{\mathrm{CE}-} & 0 & 0 & 0 & 0 & -h_x^{\mathrm{CE}-} & 0 & 0 & -2/T_{2,\mathrm{CE}} & -\Delta\omega_{\mathrm{CE}}^- & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \Delta\omega_{\mathrm{CE}}^- & -2/T_{2,\mathrm{CE}} & 0 & 0 & 0 & 0 \\
0 & -\omega_1^{\mathrm{SE}}/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\omega_1^{\mathrm{SE}}/2 & 0 & 0 & 0 & 0 & -2/T_{2,\mathrm{SE}} & -\Delta\omega_{\mathrm{DQ}} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \Delta\omega_{\mathrm{DQ}} & -2/T_{2,\mathrm{SE}} & 0 & 0 \\
0 & -\omega_1^{\mathrm{SE}}/2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \omega_1^{\mathrm{SE}}/2 & 0 & 0 & 0 & 0 & 0 & 0 & -2/T_{2,\mathrm{SE}} & -\Delta\omega_{\mathrm{ZQ}} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \Delta\omega_{\mathrm{ZQ}} & -2/T_{2,\mathrm{SE}}
\end{bmatrix}$$

For a three spin case, the problem size is reduced from a 64×64 Liouvillian operator to a 18×18 "Bloch-type" operator which results in massive time savings. The evolution operator at time $\kappa\delta t$ is given by

$$\hat{\hat{U}}_\kappa = \exp(\hat{\hat{L}}_B(\kappa\delta t) \times \delta t)$$

If we neglect the transverse relaxation times, the problem size can be further reduced to 4 x 4 using the Landau-Zener approach, in the basis $\widehat{E},\ \widehat{S}_{a,z},\ \widehat{S}_{b,z}, \widehat{I}_{n,z}$. This results in further massive time-savings but also limits the accuracy of the simulations. The relaxation can then be introduced using $\hat{\hat{R}}_1$ defined as

$$\hat{\hat{R}}_1(t) = \begin{bmatrix} 0 & 0 & 0 & 0 \\ s_{a,z}^{eq}(t)/T_{1,a}^e & -1/T_{1,a}^e & 0 & 0 \\ s_{b,z}^{eq}(t)/T_{1,b}^e & 0 & -1/T_{1,b}^e & 0 \\ s_{n,z}^{eq}(t)/T_1^n & 0 & 0 & -1/T_1^n \end{bmatrix}.$$

Then

$$\hat{\hat{U}}_\kappa = \exp(\hat{\hat{R}}_1(\kappa\delta t) \times \delta t)\hat{\hat{U}}_{\mathrm{LZ},\kappa}^{\mu\mathrm{w}}\hat{\hat{U}}_{\mathrm{LZ},\kappa}^{\text{D-J}}\hat{\hat{U}}_{\mathrm{LZ},\kappa}^{\mathrm{CE}}\hat{\hat{U}}_{\mathrm{LZ},\kappa}^{\mathrm{SE}}$$

where the LZ operator is calculated at each step and applied if two energy levels cross.

C. Effect of Electron dipolar couplings on $\epsilon_B = f(T_{\mathrm{B}})$

Figure 1 represents the effect of the electron dipolar interaction on the relation between ϵ_B and T_B. When $D_{a,b}$ in creases, the build up becomes shorter, and a much higher polarization can be obtained for the same parameters. The relation $\epsilon_B = aT_B + b$ holds, and a is at least a function of the dipolar interaction.

[1] K. R. Thurber and R. Tycko, J. Chem. Phys. **137**, 084508 (2012).
[2] F. Mentink-Vigier, U. Akbey, Y. Hovav, S. Vega, H. Oschkinat, and A. Feintuch, J. Magn. Reson. **224**, 13 (2012).

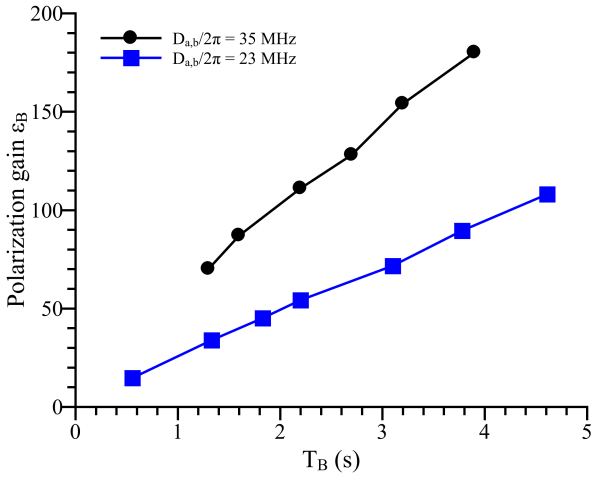

Figure 1. Effect of the electron dipolar coupling on the final ϵ_B for $D_{a,b}/2\pi = 23$ MHz (blue curve) and $D_{a,b}/2\pi = 35$ MHz (black curve). Calculations performed for TOTAPOL geometry with $\omega_1/2\pi = 0.85$ MHz, $T_1^e = 0.3$ ms, $T_2^e = 1$ μs, $A_{1,a}/2\pi = 3$ MHz, $\omega_{\mu w}/2\pi = 263.45$ GHz, $B_0 = 9.394$ T, $\nu_r = 8$ kHz. The bulk relaxation times was $T_{1,Bulk}^n = 30$ s.

[3] F. Mentink-Vigier, D. Shimon, V. Mugnaini, J. Veciana, A. Feintuch, M. Pons, S. Vega, and D. Goldfarb, Phys. Chem. Chem. Phys. **16**, 19218 (2014).
[4] M. H. Levitt and L. Di Bari, Phys. Rev. Lett. **69**, 3124 (1992).
[5] T. Levante and R. Ernst, Chem. Phys. Lett. **241**, 73 (1995).
[6] J. van Houten, W. T. Wenckebach, and N. Poulis, Phys. B+C **92**, 210 (1977).
[7] K.-N. N. Hu, G. T. Debelouchina, A. A. Smith, and R. G. Griffin, J. Chem. Phys. **134**, 125105 (2011).
[8] Y. Hovav, A. Feintuch, and S. Vega, J. Magn. Reson. **214**, 29 (2012).
[9] T. V. Can, Q. Ni, and R. G. Griffin, J. Magn. Reson. **253**, 23 (2015).
[10] F. Mentink-Vigier, U. Akbey, H. Oschkinat, S. Vega, and A. Feintuch, J. Magn. Reson. **258**, 102 (2015).
[11] B. Corzilius, A. A. Smith, and R. G. Griffin, J. Chem. Phys. **137**, 054201 (2012).
[12] F. Mentink-Vigier, S. Paul, D. Lee, A. Feintuch, S. Hediger, S. Vega, and G. De Paëpe, Phys. Chem. Chem. Phys. **17**, 21824 (2015).